START

0034434

WHC-EP-0474-11

Quarterly Report on Ferrocyanide Safety Program for the Period Ending December 31, 1993

J. E. Meacham
R. J. Cash
G. T. Dukelow

Date Published
February 1994

Prepared for the U. S. Department of Energy
Office of Environmental Restoration
and Waste Management

Westinghouse Hanford Company P.O. Box 1970 Richland, Washington 99352

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

Date Received: 2/4/94 KMB	INFORMATION RELEASE REQUEST	Reference: WHC-CM-3-4

Complete for all Types of Release

Purpose		ID Number (include revision, volume, etc.)
[] Speech or Presentation	[] Reference	WHC-EP-0474-11
[] Full Paper (Check only one suffix)	[X] Technical Report	List attachments.
[] Summary	[] Thesis or Dissertation	
[] Abstract	[] Manual	
[] Visual Aid	[] Brochure/Flier	
[] Speakers Bureau	[] Software/Database	Date Release Required
[] Poster Session	[] Controlled Document	2-3-94
[] Videotape	[] Other	

Title	Unclassified Category	Impact Level
Quarterly Report on Ferrocyanide Safety Program for the Period Ending December 31, 1993	UC-600	4

New or novel (patentable) subject matter? [X] No [] Yes
If "Yes", has disclosure been submitted by WHC or other company?
[] No [] Yes Disclosure No(s).

Information received from others in confidence, such as proprietary data, trade secrets, and/or inventions?
[X] No [] Yes (Identify)

Copyrights? [X] No [] Yes
If "Yes", has written permission been granted?
[] No [] Yes (Attach Permission)

Trademarks?
[X] No [] Yes (Identify)

Complete for Speech or Presentation

Title of Conference or Meeting	Group or Society Sponsoring

Date(s) of Conference or Meeting	City/State	Will proceedings be published? [] Yes [] No Will material be handed out? [] Yes [] No

Title of Journal

CHECKLIST FOR SIGNATORIES

Review Required per WHC-CM-3-4	Yes	No	Reviewer - Signature Indicates Approval Name (printed)	Signature	Date
Classification/Unclassified Controlled Nuclear Information	[]	[X]			
Patent - General Counsel	[X]	[]	S. W. Berglin	S W Berglin	2/2/94
Legal - General Counsel	[X]	[]	S. W. Berglin		
Applied Technology/Export Controlled Information or International Program	[]	[X]			
WHC Program/Project	[X]	[]	R. J. Cash	R J Cash	2-1-94
Communications	[X]	[]	W. P. Whiting	WP Whiting	2-2-94
RL Program/Project	[X]	[]	R. F. Christensen	R F Christensen	2/4/94
Publication Services	[X]	[]	~~C. J. Forbes~~	M. L. Barta	2-4-94
Other Program/Project	[]	[X]			

Information conforms to all applicable requirements. The above information is certified to be correct.

	Yes	No
References Available to Intended Audience	[X]	[]
Transmit to DOE-HQ/Office of Scientific and Technical Information	[X]	[]

Author/Requestor (Printed/Signature) Date
J. E. Meacham J E Meacham 2/1/94

Intended Audience
[] Internal [] Sponsor [X] External

Responsible Manager (Printed/Signature) Date
R. J. Cash R J Cash 2-1-94

INFORMATION RELEASE ADMINISTRATION APPROVAL STAMP

Stamp is required before release. Release is contingent upon resolution of mandatory comments.

APPROVED FOR RELEASE OFFICIAL KMB 2/4/94

Date Cancelled	Date Disapproved

Available to the U.S. Department of Energy
and its contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
(615) 576-8401

Available to the public from the U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650

Printed in the United States of America

DISCLM-1.CHP (1-91)

THIS PAGE INTENTIONALLY
LEFT BLANK

QUARTERLY REPORT ON FERROCYANIDE SAFETY PROGRAM FOR THE PERIOD ENDING DECEMBER 31, 1993

J. E. Meacham
R. J. Cash
G. T. Dukelow

EXECUTIVE SUMMARY

This is the eleventh quarterly report on the progress of activities addressing safety issues associated with Hanford Site high-level radioactive waste tanks that contain ferrocyanide compounds. In the presence of oxidizing materials, such as nitrates or nitrites, ferrocyanide can be made to explode in the laboratory by heating to high temperatures [above 285 °C (545 °F)]. In the mid 1950s, approximately 140 metric tons of ferrocyanide were added to waste now stored in underground high-level radioactive waste tanks.

An implementation plan (Cash 1991) responding to the Defense Nuclear Facilities Safety Board Recommendation 90-7 (FR 1990) was issued in March 1991 describing the activities that were planned and underway to address each of the six parts of Recommendation 90-7. A revision to the original plan (Borsheim et al. 1992) was transmitted to the U.S. Department of Energy by Westinghouse Hanford Company in December 1992, and subsequently to the Defense Nuclear Facilities Safety Board in 1993. The implementation plan was updated and revised this quarter and re-released as the ferrocyanide safety program plan (Borsheim et al., 1993a). The program plan still addresses the six parts of Recommendation 90-7; however, it also includes all work in the Ferrocyanide Safety Program. This quarterly report is reported against the new program plan.

Milestones completed this quarter include (1) an update of the ferrocyanide program plan; (2) a draft safety criteria document that provides the technical basis for closure of the Ferrocyanide Unreviewed Safety Question (USQ); (3) application of an improved heat load model on ferrocyanide tank 241-BY-104; (4) public release of a report on heat loads for six ferrocyanide tanks; (5) a report calculating the heat loads in all the ferrocyanide tanks using tank dome space temperature measurements; (6) a letter report examining risers in ferrocyanide tanks for possible liquid observation well insertion and assessing the effects of liquid observation well material on neutron probe performance; and (7) a mathematical evaluation, by Fauske and Associates, Inc., of waste dry out by theoretical hot spots.

A draft report defining criteria for safe storage of ferrocyanide waste in Hanford Site tanks was submitted to the U.S. Department of Energy this quarter (Postma et al., 1993). The report, Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks (WHC-EP-0691), provides the technical basis for closure of the Ferrocyanide unreviewed safety question and represents a key step in meeting Safety Initiative 2s, closure of the Ferrocyanide Unreviewed Safety Question by January 31, 1994.

An improved heat load model was used to reexamine the heat load in the ferrocyanide Tank 241-BY-104. A report describing the new model and the analysis of 241-BY-104 was released this quarter as Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104, WHC-EP-0669 (McLaren 1993a).

The integrated heat loads for all the ferrocyanide tanks were calculated this quarter using dome space temperature measurements (Crowe et al., 1993). The report, Estimation of Heat

<u>Load in Waste Tanks Using Average Vapor Space Temperatures</u>, WHC-EP-0708, was publicly released. Heat loads calculated from tank dome space temperatures correlated closely with other methods previously used to determine selected heat loads.

A data quality objectives document, <u>Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process</u>, WHC-EP-0728 (Buck et al., 1993), was publicly released this quarter. The report provides a statistical basis for the number of cores required to characterize ferrocyanide tank waste. The report concluded that two cores taken from representative areas of the tank are sufficient to determine fuel and moisture concentrations.

A letter report was completed this quarter as part of in situ moisture monitoring technology development (Toffer 1993). The report examined risers in ferrocyanide tanks for possible liquid observation well insertion and assessed the effects of potential liquid observation well materials on neutron probe performance. Of the materials modeled, aluminum and zirconium displayed the best sensitivity for moisture monitoring.

Preliminary data from core samples obtained from Tank 241-T-107 were received this quarter. None of the segments containing sludge exhibited exothermic activity during differential scanning calorimetry analysis. Total cyanide concentrations in the samples were very low; the maximum concentration found for any of the segments was 106 $\mu g/g$. Moisture concentrations in the segments ranged between 17 and 60 wt%.

Adsorption/desorption tests at Nuclear Consulting Services Inc. on In Farm simulant indicated that the sludge still retains substantial free water when exposed to relative *humidities of 30, 50, 70, and 90 percent (%). The simulant retained 4.1 wt%, 10.6 wt%, 31.3 wt%, and 65.4 wt% free water, respectively, at equilibrium for these relative humidities. This is in addition to the ~4.8 wt% of bound water also retained in the sludge.*

Aging experiments performed this quarter revealed that dissolution and hydrolysis of ferrocyanide simulants can still occur at a pH of 10, albeit at a substantially reduced rate. Ammonia concentrations found in these experiments were approximately two orders of magnitude lower than for similar durations using 4.0 molar caustic (NaOH). Experiments next quarter will be allowed to run longer to determine if the aging process will continue in the pH 10 experiments.

Analyses of T Plant flowsheet ferrocyanide simulant were conducted this quarter. Fuel concentration in the T Plant simulant was 8.8 wt% [as $Na_2NiFe(CN)_6$], slightly higher than the 8.3 wt% found in U Plant simulant. T Plant simulant did not support propagating reactions during adiabatic calorimetry testing by Fauske and Associates, Inc.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TERMS

AA	Atomic Absorption
ARC	Accelerating Rate Calorimetry
CASS	Computer Automated Surveillance System
CPAC	Center for Process Analytical Chemistry
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy, Richland Operations Office
DOE-HQ	U.S. Department of Energy, Headquarters
DQO	Data Quality Objectives
EIS	Environmental Impact Statement
EA	Environmental Assessment
FAI	Fauske and Associates, Inc.
FTIR	Fourier Transform Infrared
FY	Fiscal Year
g	Gravities
GAO	General Accounting Office
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
IR	Infrared
ISB	Interim Safety Basis
LANL	Los Alamos National Laboratory
LFL	Lower Flammability Limit
LOW	Liquid Observation Well
MCNP	Monte Carlo Neutron Photon [Model]
μg	Micrograms
μm	Micrometers
MIT	Multifunctional Instrument Tree
NIR	Near Infrared
PNL	Pacific Northwest Laboratory
ppm	Parts Per Million
RSST	Reactive Systems Screening Tool (small adiabatic calorimeter at FAI)
RH	Relative Humidity
SA	Safety Assessment
SAR	Safety Analysis Report
SRL	Savannah River Laboratory
SST	Single-Shell Tank
TAP	Tanks Advisory Panel
TC	Thermocouple
TMACS	Tank Monitor and Control System
TPA	Tri-Party Agreement, *Hanford Federal Facility Agreement and Consent Order*
USQ	Unreviewed Safety Question
VSP	Vent Sizing Package (large adiabatic calorimeter at FAI)

This page intentionally left blank.

1.0 INTRODUCTION

1.1 PURPOSE

This quarterly report provides a status of the activities underway at the Hanford Site on ferrocyanide waste tank safety issues, as requested by the Defense Nuclear Facilities Safety Board (DNFSB) in their Recommendation 90-7 (FR 1990). In March 1991, a DNFSB implementation plan (Cash 1991) responding to the six parts of Recommendation 90-7 was prepared and sent to the DNFSB. The implementation plan was updated and released to the U.S. Department of Energy, Richland Operations Office (DOE-RL), as a draft program plan in December 1993 (Borsheim et al., 1993a). This and future quarterly reports will be reported against this new program plan. All activities in the revised program plan are underway or have been completed, and the status of each is described in Section 4.0 of this report.

1.2 QUARTERLY HIGHLIGHTS

- The ferrocyanide program plan was updated this quarter (Borsheim et al., 1993a). The program plan describes current and expected future work in the Ferrocyanide Safety Program through resolution of the Ferrocyanide Safety Issue. Work for the Ferrocyanide Safety Program will be reported against the new program plan on a quarterly basis.

- A draft report defining criteria for safe storage of ferrocyanide waste in Hanford Site tanks was submitted to the U.S. Department of Energy (DOE) this quarter (Postma et al., 1993). The report, titled *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks* (WHC-EP-0691), provides the technical basis for closure of the Ferrocyanide Unreviewed Safety Question (USQ).

- The final report on ultra high-pressure bore head testing has been approved and all the equipment necessary to support installation of thermocouple (TC) trees using ultra high-pressure bore heads has been obtained. However, installation was delayed as a result of the Administrative Hold. The high pressure pump that supplies the water necessary for boring was refurbished and is awaiting acceptance testing.

- An improved heat load model was used to reexamine the heat load in the ferrocyanide tank 241-BY-104. A report describing the new model and the analysis of 241-BY-104 was released this quarter as *Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104*, WHC-EP-0669 (McLaren 1993a).

- The integrated heat loads for all the ferrocyanide tanks were calculated this quarter using dome space temperature measurements. The report, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0708 (Crowe et al., 1993), was publicly released this quarter. Heat loads calculated from tank dome space temperatures correlated closely with other methods previously used to determine selected heat loads.

- A study evaluating the need for continuous gas monitoring in ferrocyanide tanks was started this quarter. Sampling data are being examined and a report examining the necessity for monitoring selected ferrocyanide tanks will be completed in March 1994.

- A data quality objectives report, *Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process*, WHC-EP-0728 (Buck et al., 1993), was publicly released this quarter. The report concluded that two full-depth cores are required to determine fuel and moisture content in ferrocyanide tanks.

- Preliminary sample data from tank 241-T-107 were received this quarter. None of the quarter segments containing sludge exhibited exothermic activity during differential scanning calorimetry analysis. Total cyanide concentration in the tank was very low; the maximum concentration found among all the quarter segments was of 106 μg/g.

- A report summarizing the progress on developing neutron diffusion technology for *in situ* moisture monitoring in Hanford Site tanks was publicly released this quarter, titled *Proof of Principle Report for In-Tank Moisture Monitoring Using an Active Neutron Probe*, WHC-EP-0695 (Watson 1993).

- A study investigating the feasibility of deploying a miniature neutron probe inside a small diameter well ($\sim$1.25 inches in diameter) was completed this quarter. The study concluded that a limited size probe can be readily designed for deployment in a cone penetrometer to measure moisture concentrations in waste tanks not equipped with liquid observation wells (LOWs). The study also estimated that 30 to 60 minutes would be required to scan a depth of 10 feet in the tank.

- A letter report was completed this quarter as part of *in situ* moisture monitoring technology development (Toffer 1993). Risers in ferrocyanide tanks were examined for possible LOW insertion, and the effects of potential LOW materials on neutron probe performance were assessed. Aluminum and zirconium yielded the best sensitivity among the modeled materials.

- Adsorption/desorption tests at Nuclear Consulting Services Inc. on In Farm simulant indicated the sludge still retains substantial free water when exposed to relative humidities of 30, 50, 70, and 90%. The simulants retained 4.1, 10.6, 31.3, and 65.4 wt% free water (respectively) at equilibrium (note: this is in addition to the ~4.8 wt% of bound water also retained in the sludge).

- Aging experiments performed this quarter revealed that dissolution and hydrolysis of ferrocyanide simulants can still occur at a pH of 10, albeit at a substantially reduced rate. Ammonia concentrations found in these experiments were approximately two orders of magnitude lower than for similar durations using 4.0 molar caustic (NaOH). Experiments next quarter will be allowed to run for longer durations to determine if the aging process will continue in the pH 10 experiments.

- Experiments on T Plant flowsheet ferrocyanide simulant were conducted this quarter. Fuel concentration in the T Plant simulant was 8.8 wt% [as $Na_2NiFe(CN)_6$], slightly higher than the 8.3 wt% found in U Plant simulant. T Plant simulant could not be made to propagate during adiabatic calorimetry testing.

1.3 REPORT FORMAT

Progress of activities under each of the six parts of DNFSB Recommendation 90-7 are arranged in the same order as the program plan (Borsheim et al., 1993a). The arrangement also follows the same order provided in the recommendation. To report on progress, each part of the recommendation is repeated in italics, followed by paragraphs explaining the scope of work on each part or subpart of the recommendation. Subheadings for each task activity report the following:

- Progress During Reporting Period
- Planned Work for Subsequent Months
- Problem Areas and Action Taken
- Milestone Status.

This page intentionally left blank.

2.0 BACKGROUND

Various radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the mid 1940s. During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period, and to minimize the need for constructing additional storage tanks, Hanford Site scientists developed a process to scavenge ^{137}Cs from tank waste liquids. In implementing this process, approximately 140 metric tons (154 tons) of ferrocyanide were added to waste that was later routed to some Hanford Site SSTs. In 1991, based on available information, 24 tanks were assigned to the Ferrocyanide Watch List using the criterion that they originally received inventories of at least 1,000 g-moles as the $Fe(CN)_6^{4-}$ anion.

Ferrocyanide, in the presence of oxidizing material such as sodium nitrate and/or nitrite, can propagate and sometimes explode in the laboratory by heating it to high temperatures or by an electrical spark of sufficient energy. Under laboratory conditions deliberately created to enhance the potential for reactions, significant exothermic reactions can start as low as 220 °C (430 °F), but the lowest explosion temperature observed is approximately 285 °C (545 °F). The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo endothermic and exothermic reactions have not been thoroughly studied. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been underway since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs (Burger 1989; Burger and Scheele 1988). The potential consequences of a postulated ferrocyanide burn or explosion were not evaluated in the safety analyses or safety analysis reports (SAR) applicable to the Hanford Site SSTs. The SARs historically have considered an explosion from fuel/nitrate reactions as an incredible event and the consequences of incredible events are not required to be analyzed (WHC 1992).

Although not considered a part of the safety analysis for the storage of waste in the SSTs, the 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington* (HDW-EIS) (DOE 1987) did include an environmental impact analysis of potential explosions involving ferrocyanide-nitrate mixtures. The EIS postulated that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 mrem. A General Accounting Office (GAO) study (Peach 1990) postulated a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than in the DOE EIS (DOE 1987). Coupling the ferrocyanide concerns with concerns about high organic concentrations and potential hydrogen accumulations in other Hanford Site HLW tanks, the DOE established the High-Level Radioactive Waste Tanks Task Force and Tanks Advisory

Panel (TAP) in August 1990. These two groups were formed to ensure that all safety concerns with HLW tanks at DOE sites are identified and addressed in a systematic and timely manner.

The initial focus of the task force and advisory panel was on the Hanford Site flammable gas and Ferrocyanide Safety Issues. In September 1990, a special Hanford Site ferrocyanide task team was commissioned by the Westinghouse Hanford Company to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident.

The root cause of the ferrocyanide problem results from a combination of factors, beginning with the safety studies performed as precursors to using the ferrocyanide scavenging flowsheets. These studies did not include ultimate disposal of the ferrocyanide solids, and were not performed to the conservative standards used today, because the studies did not discuss the risk of adding ferrocyanide to waste tanks. In addition, no rigorous inventory was kept of the ferrocyanide or other chemicals added to the tanks. Subsequent safety studies either were not performed, or were performed to less conservative standards, to demonstrate that other chemicals would not increase the level of risk. Monitoring systems for designated single-shell tanks (SSTs), such as temperature measurement instrumentation, were allowed to be disconnected and fall into disrepair because the potential hazard was not highlighted.

Although the HDW-EIS (DOE 1987) estimated the consequences from a postulated explosion, the GAO disagreed with the assumptions of that document. Work performed by Pacific Northwest Laboratory (PNL) in 1984-85 identified a potential safety problem, but no funding was provided until 1989 to study this Safety Issue. An additional issue was subsequently communicated about the assumed radioactive material source term (release fraction) resulting from a postulated explosion (Peach 1990).

In October 1990 (Deaton 1990), the Ferrocyanide Issue was declared an USQ[1] because the safety envelope for these tanks was no longer bounded by the existing safety analysis report (RHO 1986). In 1991, using process knowledge, process records, transfer records, and log books, 24 tanks were identified at the Hanford Site as potentially containing 1,000 g-mole

---

[1]An Unreviewed Safety Question, as defined by DOE Orders 5480.5 (DOE 1986) and 5480.21 (DOE 1991), is determined as follows. "A proposed change, test or experiment shall be deemed to involve an USQ if the following apply:

a. The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety, evaluated previously by safety analysis will be significantly increased, or

b. A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."

(465 lb) or more of ferrocyanide [as the $Fe(CN)_6^{4-}$ anion]. These tanks were placed on a Ferrocyanide Watch List because of the USQ.

Work in and around any of the ferrocyanide tanks requires detailed planning, including preparing the supporting safety and environmental documentation and approval by DOE top management. These restrictions are imposed to ensure that appropriate precautions are taken to minimize the potential safety and environmental impacts associated with the ferrocyanide hazard. The need to evaluate the hazards and ensure that appropriate controls are implemented has, to date, increased the time required to complete work or install equipment in the tanks. Re-examination of the historical records (Borsheim and Simpson 1991) indicated that 6 of the 24 tanks do not contain the requisite 1,000 g-moles of ferrocyanide and should not have been included on the Watch List. Four of the 6 tanks were removed from the Watch List in June 1993 (Meacham et al., 1993a) and removal of the other two tanks is pending (Borsheim et al., 1993b).

This page intentionally left blank.

3.0 FERROCYANIDE PROGRAM SAFETY DOCUMENTATION

The USQ process depends on an authorization basis that describes those aspects of the facility design basis and operational requirements relied on by DOE to authorize operation. The authorization basis is described in documents such as facility SARs and other safety analyses, hazard classification documents, technical safety requirements, DOE issued safety evaluation reports, and facility-specific commitments, such as the safety assessments (SAs) and the Interim Safety Basis (ISB) (Wagoner 1993). The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the authorization basis. Until the USQ is closed, proposed intrusive activities that may impact the safety of the ferrocyanide tanks must be assessed for potential safety and environmental consequences. Furthermore, these activities must be authorized by DOE.

A strategy for closing the USQ and resolving the Safety Issue surrounding the ferrocyanide wastes was developed by DOE and Westinghouse Hanford Company and presented to the DNFSB in August 1993 (Grumbly 1993). The strategy contains two key steps: (1) developing criteria for safety categories that rank the hazard for each tank, allowing closure of the USQ, and (2) confirmation and final placement of each tank into one of the categories based on core sampling and characterization of the tank contents.

As part of the accelerated Safety Initiatives (O'Leary 1993), closure of the Ferrocyanide USQ was moved forward from September 1994 to January 1994. This, coupled with the new strategy for USQ closure, resulted in an improved schedule for USQ closure. The USQ can be closed formally by DOE on the basis of documented criteria. Resolving the Ferrocyanide Safety Issue will be a follow-on effort that requires the sampling of the ferrocyanide tank waste to quantify the potential for hazardous reactions.

Ferrocyanide Program Plan. The ferrocyanide program plan was updated this quarter and submitted for DOE approval (Borsheim et al., 1993a). The program plan describes all of the current and anticipated future work in the ferrocyanide program. Schedules showing program activities leading to eventual safety issue resolution by fiscal year (FY) 1997 are presented in the program plan. Work in the ferrocyanide program will be reported against the new program plan on a quarterly basis (see Section 5.0 for schedules and work status).

Safety and Environmental Assessments. SAs are documents prepared to provide the technical basis to assess the safety of a proposed activity and to provide proper controls to maintain safety. The SA, along with the accompanying Environmental Assessment (EA) for that operation, provides the basis for DOE authorization of the proposed activities. The authorization basis for previously analyzed intrusive tank operations was combined into one document, the ISB, which was approved by DOE in November 1993 (Wagoner 1993).

SAs have been completed for vapor space sampling of all ferrocyanide tanks, waste surface sampling, push-mode core sampling, TC tree installation in sound tanks, and removal of pumpable liquid from leaking tanks (interim stabilization). A discussion of the interim stabilization SA is presented in Section 4.6.1.

A decision was made to revise the existing SA for installing TC trees in sound (non-leaking) ferrocyanide tanks so that installation in leaker tanks was also addressed. A study to evaluate and identify alternative methods for installation of TC trees in assumed leaker ferrocyanide tanks was completed. The previous method used relatively large volumes of water to sluice the TC tree through the waste. An ultra high pressure concept that uses minimal quantities of water was chosen for final testing and design. The SA was first transmitted to DOE in November 1993, and several revisions have been made to incorporate DOE comments.

The EA for installation of instrument trees into the 14 "assumed leaker" ferrocyanide tanks has been incorporated into the generic EA covering operations for Watch List tanks. A draft of the generic EA was sent to the U.S. Department of Energy, Headquarters (DOE-HQ) this quarter and is awaiting final approval. The predecisional safety assessment addressing installation of instrument trees into assumed leaker tanks was sent to the DOE for review and approval on November 30, 1993.

A SA for rotary-core sampling of ferrocyanide and other Watch List tanks that contain hard waste (e.g., saltcake) is necessary. The most recent revision of the SA for rotary-core sampling was sent to DOE in October 1993 and is waiting DOE-HQ approval. The rotary drill system is expected to be deployed for field operation in March 1994.

Hazard Assessment. The effort to update the ferrocyanide hazards assessment document was redirected in June 1993 toward developing a safety criteria document supporting closure of the Ferrocyanide USQ and a technical basis document supporting resolution of the Ferrocyanide Safety Issue. At that time, agreement was reached between DOE and Westinghouse Hanford on the approach for closure of the USQ and resolving the Safety Issue.

An updated ferrocyanide hazards assessment, now referred to as a technical basis document, will not be started until enough information is available for resolving the Ferrocyanide Safety Issue. Technical information from all Ferrocyanide Safety Program tasks will be incorporated into this document. This document will be completed in FY 1995 to support Safety Issue resolution for the four C Farm tanks. An update of the document may be necessary in FY 1997 to support Safety Issue resolution for the remaining 14 tanks.

Dose Consequences. A report describing the consequences of hypothetical burns of differing sizes in a ferrocyanide tank is being prepared. The report will be prepared by July 1994 and will satisfy the milestone originally set for September 30, 1993.

Closure of the Ferrocyanide USQ. The Ferrocyanide USQ criteria document draft (Postma et al. 1993) was submitted for DOE review and approval on December 1, 1993. Based on the knowledge gained from simulant studies and theoretical analyses, safety categories and safety criteria were delineated to meet the interim safe storage safety objective. The primary safety objective is to maintain waste in a state that prevents chemical reactions that have the potential for radiation doses or toxic exposure (either onsite or offsite) more than applicable limits or guidelines, and damage to the tank that compromises its ability to store high-level waste safely. The primary safety objective is met by imposing a more stringent secondary objective; that is, no sustainable rapid exothermic ferrocyanide reaction be possible, regardless of the severity of its consequences. A sustainable reaction is one that can spread beyond a local ignition source. A rapid reaction is one that generates heat faster than it can be removed by conduction; it excludes the slow degradation reactions believed to be occurring over a period of years.

Two key safety questions were used to identify three safety categories. The questions were developed on the basis of the current understanding of the ferrocyanide waste hazard.

Question 1: *Is a significant exothermic reaction possible during interim storage?*

The word *significant* in this question is defined by reference to the safety objective. A *significant* reaction would have consequences greater than permitted by the safety objective. The phrase *possible during interim storage* in Question 1 means conditions that could theoretically occur if no controls were placed on tank operations. This no control stipulation allows for such possible but unlikely events as dryout and the introduction of local initiators. The no control stipulation does not cover processes and operations that could be imposed in future efforts directed at final disposal of the waste.

If the answer to Question 1 is no, then the waste can be safely stored without human intervention. If the answer to Question 1 is yes, then a second key question is posed.

Question 2: *Is a significant exothermic reaction possible under present conditions of waste moisture content?*

If the answer to this question is no, then the safety objective can be met by assuring that the waste maintains moisture content above a level that prevents significant exothermic reactions. If the answer to this question is yes, then the primary safety objective can be met only by imposing controls that avoid conditions that could initiate a reaction. The more stringent secondary objective cannot be met if the answer to Question 2 is yes.

Answers to these two key safety questions led to the definition of three safety categories: SAFE, CONDITIONALLY SAFE, and UNSAFE. The SAFE category corresponds to a "no" answer to key safety Question 1 (i.e., that a significant reaction is not possible during interim storage). The safety objective can be met by a hypothetical unattended operational mode; no special requirements for monitoring and controls are imposed by the presence of ferrocyanide.

The CONDITIONALLY SAFE category corresponds to a yes answer to key safety Question 1, followed by a no answer to key safety Question 2. The wastes in this category are safe on the condition that moisture content be maintained at or above a definable critical level. In reaction phenomenology, the requirements are the same as for the SAFE category, except that a waste moisture level above a critical value applies. Therefore, propagating reactions can be ruled out for this safety class.

The UNSAFE category corresponds to yes answers to both key safety questions. For wastes in this category, a reaction initiated at a local site could propagate through a significant quantity of waste. Accidents would be prevented by imposing controls that avoid conditions that could initiate a reaction. Storage of wastes in this category is inconsistent with the more stringent secondary safety objective, because significant reactions cannot be ruled out. A change in waste state would be required to ensure that waste storage met the level of safety required by the secondary safety objective.

The parameters important for exothermic oxidation/reduction reactions involving ferrocyanide are fuel, oxidant, and moisture concentrations, and temperature. Criteria were established on fuel concentration, moisture content, and temperature that allow the tanks to be ranked into the three safety categories.

I. LEVEL 1 - SAFE

Concentration of fuel:	≤ 8 wt% sodium nickel ferrocyanide on an energy equivalent basis (i.e., ≤ 115 cal/g)
Concentration of water:	Not limiting
Concentration of oxidizers:	Not limiting
Temperature of waste:	Not limiting

II. LEVEL 2 - CONDITIONALLY SAFE

Concentration of fuel:	> 8 wt% sodium nickel ferrocyanide on an energy equivalent basis
Concentration of water:	≥ 0 to 24 wt%
Concentration of oxidizers:	Not limiting
Temperature of waste:	≤ 90 °C

III. LEVEL 3 - UNSAFE

Criteria for SAFE and CONDITIONALLY SAFE are not met; a modification in waste state is required to remove a tank from the UNSAFE class.

It is important to note three features of the criteria. The fuel criterion is determined on an energy equivalent basis that accounts for possible contributions from other potential fuel sources, such as sulfide or organics. The moisture criterion is not fixed at one value, but increases linearly from 0 at 8 wt% fuel, to 24 wt% at 26 wt% fuel. Waste that contains, for example, 8.3 wt% fuel is not required to have 24 wt% water; it requires only 0.4 wt% water. Temperature is not a primary criterion, and is set at 90 °C to preclude rapid moisture loss in the waste. Actions to cool the waste would be taken long before temperatures in the tank increased to 90 °C (12). Based on information from the waste simulants and core sample analyses, all of the ferrocyanide tanks are currently placed in either the SAFE or CONDITIONALLY SAFE categories.

- **Milestone Status**

  - **December 1, 1993**: Submit, for DOE review, a draft ferrocyanide safety criteria document that defines safe storage of ferrocyanide waste. This milestone was completed on schedule by transmittal of the document, *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*, WHC-EP-0691 (Postma et al., 1993).

  - **December 17, 1993**: Submit an update of the ferrocyanide program plan to DOE for approval. The document, *Program Plan for Evaluation of the Ferrocyanide Waste Tank Safety Issue at the Hanford Site*, WHC-EP-0721 (Borsheim et al., 1993a), was transmitted to DOE on schedule.

  - **January 31, 1993**: Requested DOE approval to close Ferrocyanide USQ. This is two months earlier than called for in Tri-Party Agreement (TPA) milestone M-40-14.

  - **June 24, 1994**: Issue an Interim Safety Basis Level 1 report to DOE which provides an updated safety basis for safe operation of ferrocyanide tanks.

  - **July 29, 1994**: Issue an update of the ferrocyanide hazards assessment document. This milestone will be deferred to FY 1995 or canceled pending disposition of the Ferrocyanide USQ closure document and the timing for resolving the Safety Issue.

  - **July 29, 1994**: Complete a final report, approved for public release, on effects and consequences of various *in situ* ferrocyanide tank waste burns.

  - **August 31, 1995**: Issue technical basis document supporting Safety Issue resolution for C Farm tanks. Recommend Safety Issue resolution for C Farm tanks.

  - **February 29, 1996**: DOE approval to remove C Farm tanks from the Watch List. Safety Issue resolved for C Farm ferrocyanide tanks.

  - **January 31, 1997**: Technical basis revised to support Safety Issue resolution for the remaining 14 tanks. Recommend Safety Issue resolution for all remaining ferrocyanide tanks.

  - **September 30, 1997**: DOE approval to remove all ferrocyanide tanks from the Watch List. Ferrocyanide Safety Issue resolved.

This page intentionally left blank.

4.0 DESCRIPTION OF ACTIVITIES

This section follows the format of the program plan (Borsheim et al., 1993a) and describes all of the work associated with the Ferrocyanide Safety Program. Each task activity is described relative to the applicable DNFSB Recommendation (90-7.1 through 90-7.6). The specific recommendation is given, followed by a summary of activities underway to respond to the recommendation (if not already closed out).

4.1 ENHANCED TEMPERATURE MEASUREMENT

"Immediate steps should be taken to add instrumentation as necessary to the SSTs containing ferrocyanide that will establish whether hot spots exist or may develop in the future in the stored waste. The instrumentation should include, as a minimum, additional thermocouple trees. Trees should be introduced at several radial locations in all tanks containing substantial amounts of ferrocyanide, to measure the temperature as a function of elevation at these radii. The use of infrared techniques to survey the surface of waste in tanks should continue to be investigated as a priority matter, and on the assumption that this method will be found valuable, monitors based on it should be installed now in the ferrocyanide bearing tanks."

4.1.1 Instrument Trees

DNFSB Recommendation 90-7.1 requests that actions be taken to add instrumentation to the ferrocyanide waste tanks to measure waste temperatures and to determine if hot spots exist or may develop.

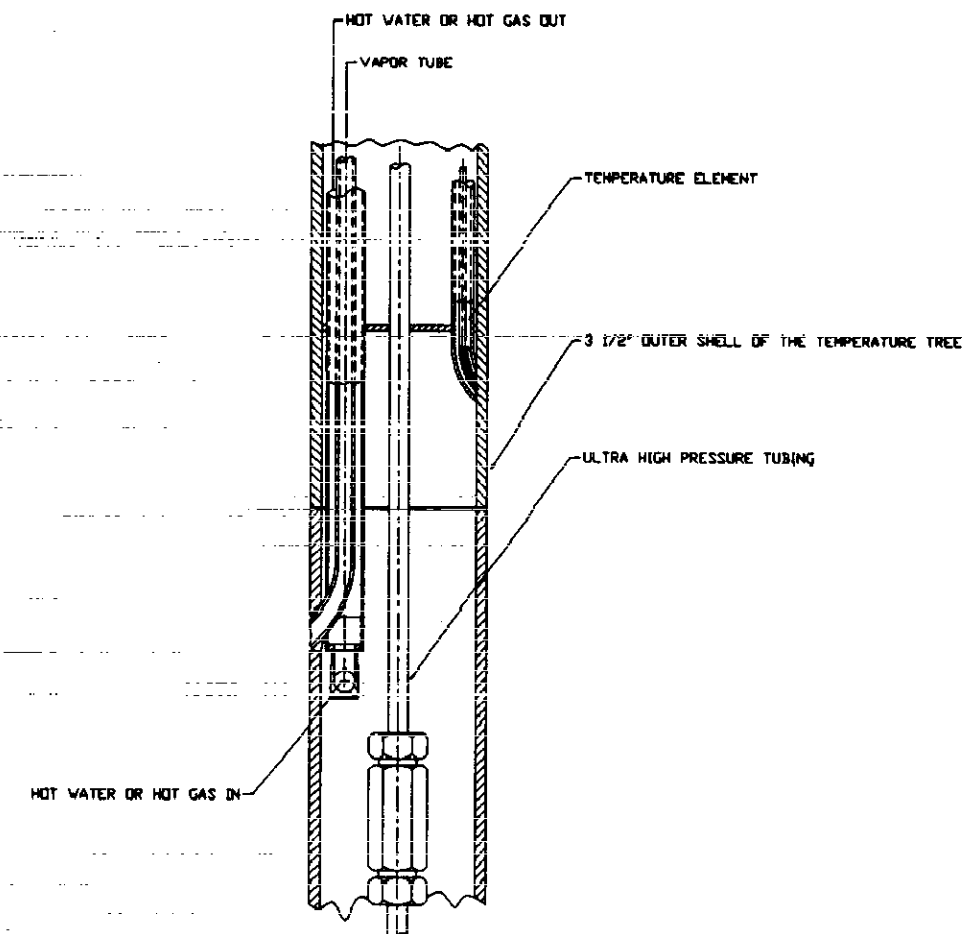
A strategy was initially developed to provide the temperature instrumentation necessary to monitor conditions in five high-concern waste tanks on an expedited basis. The strategy was to (1) repair the existing TC elements (where possible); (2) install new instrument trees that would be fabricated from existing drawings; and (3) install multifunctional instrument trees (MITs) in those tanks that have a limited number of risers available. The MITs would provide temperature monitoring, the capability for gas sampling at three elevations, possible pressure monitoring, and access for deployment of fiber optics inside the tanks if desired. The TC trees would provide temperature monitoring but may not provide the option to obtain any additional data. This strategy was later revised to include only repair of existing TC trees and installation of new instrument trees or replacement of TC elements where necessary. There are no plans to install MITs in the ferrocyanide tanks at this time. To date, TC trees have been installed in 10 non-leaker ferrocyanide tanks.

- **Progress During Reporting Period.** Instrument trees with heated vapor sampling tubes (Figure 4-1) have been fabricated for the first four assumed leaker tanks. Ultra high-pressure bore heads were installed on two of the new instrument trees this quarter.

The final report for the ultra high-pressure bore head testing has been approved and all the equipment necessary to support installation of TC trees using ultra high-pressure bore heads has been secured. The high pressure pump that supplies the water necessary for boring was refurbished and is awaiting acceptance testing.

Planning for installation of instrument trees in the assumed leaker tanks has continued; however, installation was delayed as a result of the Administrative Hold placed on tank farm operations in August 1993 (Meacham et al., 1993a).

Figure 4-1. Vapor Sampling Tube for New Thermocouple Tree Design.



Work was initiated this quarter on a document that would describe the criteria for upgraded temperature monitoring capabilities in ferrocyanide tanks. This is a recently established TPA milestone (M-40-02A).

- **Planned Work for Subsequent Months.** High-pressure bore heads will be installed into the two remaining instrument trees. Instrument trees will be installed into four assumed leaker tanks (241-BY-107, -108, 241-C-111, and 241-TY-104). Four additional instrument trees will be fabricated.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **June 30, 1994**: Complete installation of the first four TC trees in assumed leaker tanks.

  - **September 30, 1994**: Complete installation of instrument trees in assumed leaker ferrocyanide tanks. Installations have been delayed because of the Administrative Hold and completion of this milestone was slipped to December 1994. This milestone also addresses the September 1994 TPA milestone M-40-028, installation of six TC trees in ferrocyanide tanks.

  - **September 30, 1994**: Develop criteria for upgraded temperature monitoring capabilities in ferrocyanide tanks (TPA milestone M-40-02A).

4.1.2 Upgrades to Existing Temperature Monitoring Instrumentation

This task determined the operability and accuracy of previously installed TC elements in the original 24 ferrocyanide tanks at the Hanford Site. The original and newly installed TCs now provide temperature readings for the ferrocyanide tanks.

Field measurements were taken in 1991 on each TC element in the then-existing trees to determine the resistance and voltage across the junction and across each lead to ground. The exact condition of each TC was determined by resistance and voltage measurements (Bussell 1992). This work was completed in FY 1991 with a total of 265 TCs being evaluated. Work in FY 1992 focused on repair and recovery of 92 TCs that were found to be failed or marginal in performance. This task was completed in FY 1992.

- **Progress During Reporting Period.** No progress was required or planned.

- **Planned Work for Subsequent Months.** None.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.** This task is considered to be complete.

4.1.3 Hot Spot Thermal Modeling

The decay of radioactive materials in Hanford Site waste tanks generates heat. A concern has been whether an exothermic excursion and local propagation might occur within the ferrocyanide waste if there was a sufficient concentration of ferrocyanide and a high enough temperature present. There is usually only one or two instrument trees in each ferrocyanide tank, and the trees are not always at the same location. Consequently, there is some question if significant heat generation could exist in these tanks and not be detected. This task models and analyzes the available temperature data from the ferrocyanide tanks in order to determine the heat load and temperatures as a function of depth and radial location. Sensitivity and parametric analyses are included to determine the magnitude of hot spots that would have to exist within the waste to cause a propagating reaction to occur.

State-of-the-art validated computer codes are used in the modeling. They are benchmarked with existing data and employ two- and three-dimensional capabilities. Both steady-state and transient models are used. The intent of this work is to determine accurate heat loads for each ferrocyanide tank and to model hypothetical hot spots.

- **Progress During the Reporting Period.** Development of an improved model for thermal analysis of the ferrocyanide waste storage tanks has been completed, and the model was used to reanalyze tank 241-BY-104. This model takes into account known data concerning soil moisture, with resulting thermal conductivity changes at the various locations around the tanks and the measured temperature accuracies. It was determined that including radiant and convective heat transfer to the walls of the tank offer little improvement in accuracy. The heat load and temperature history of the tanks are included since it has been found that the tanks are not as close to a steady-state condition as previously supposed, and that the use of a steady state model produces values for the tank heat loads that are overly conservative. The report of the model development and tank analysis is titled *Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104*, WHC-EP-0669 (McLaren 1993), and was publicly released in December 1993.

  Integrated tank heat loads for all the ferrocyanide tanks were calculated this quarter using tank dome space temperature measurements. A report reviewing this work was publicly released this quarter as *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0708 (Crowe et al., 1993). Heat loads calculated from tank dome space temperatures correlated closely with other methods previously used for calculating heat loads for selected ferrocyanide tanks.

- **Planned Work for Subsequent Months.** The updated thermal heat transfer/heat load model will be utilized for heat load and thermal characteristics analysis of all ferrocyanide tanks. Two reports of these analyses will be prepared and issued later in FY 1994.

  Changes will be made to the report *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Waste by Hot Spots*, WHC-EP-0648, Rev. 0 (Dickinson et al., 1993), to incorporate comments received from DOE.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **April 15, 1993**: Perform detailed thermal modeling studies to (1) determine if there is enough likelihood for forming hot spots to warrant infrared scans of ferrocyanide tanks; and (2) issue a position paper on whether hot spots of concern are credible. The position paper, *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Waste by Hot Spots*, WHC-EP-0648, Rev. 0 (Dickinson et al., 1993) was issued April 15, 1993.

  - **September 17, 1993**: Complete thermal hydraulic analyses (using the updated thermal heat load model) of tank 241-BY-104 to determine heat load and conductivities of the waste contents and issue a report, available to the public, on the results of the analysis. The scope of this milestone was reduced to one tank (from four tanks) and the date slipped from November 1993 because of delays in developing the updated heat transfer/heat load model. The report, *Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104*, WHC-EP-0669, (McLaren 1993) was released December 29, 1993, to meet this milestone.

  - **December 30, 1993**. Complete and issue a report, available to the public, of corrected thermal analyses of six ferrocyanide tanks (241-BY-105, -106, -108, -110, 111, and 241-C-109). The report *Ferrocyanide Safety Program: Heat Load and Thermal Characteristics Determination for Selected Tanks*, WHC-EP-0638, (McLaren and Cash 1993) was released December 20, 1993, to meet this milestone.

  - **December 30, 1993**. Complete and issue a report to the public on the use of tank dome space temperature measurements to calculate integrated heat loads for ferrocyanide tanks. The report *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0708 (Crowe et al., 1993), was released in December 1993 to meet this milestone.

- **March 31, 1994.** Complete additional analyses and issue an update of the report *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Waste by Hot Spots* (Dickinson et al., 1993), approved for public release.

- **June 30, 1994.** Complete thermal hydraulic analyses of heat loads for nine ferrocyanide tanks (241-BY-103, -105, -106, -107, -108, -110, -111, and 241-C-109 and -112) using the updated thermal model, and issue a report for public release.

- **September 30, 1994.** Complete thermal hydraulic analyses of heat loads for all remaining ferrocyanide tanks and issue a report available for public release.

4.1.4 Infrared Scanning System

Infrared scanning systems are commercially available from numerous vendors. These systems are sensitive to changes of ± 0.3 °C (0.5 °F) or less under ideal conditions, and offer promise for mapping surface temperature profiles in the ferrocyanide tanks. Thermal modeling performed on ferrocyanide tank 241-BY-104 suggested that, if hot spots with temperatures of concern are possible, surface temperature differences might be great enough to be detected by infrared mapping.

The position paper on the credibility of hot spots and the need for further infrared (IR) scanning was completed and issued, *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Tank Waste by Hot Spots* (Dickinson et al., 1993). This paper examined potential concentration mechanisms and determined the degree of concentration required to produce temperatures high enough to dry the ferrocyanide waste. The paper concluded that such concentrations were incredible. Based on this report, Westinghouse Hanford recommended to the DOE-RL that no further planning be pursued for infrared scans for the purpose of detecting hot spots.

- **Progress During the Reporting Period.** None.

- **Planned Work for Subsequent Months.** A draft report on the infrared scans of tank 241-S-110, *Application of Infrared Imaging in Ferrocyanide Tanks*, (WHC-EP-0593) was submitted to DOE in January 1993. This report is still awaiting DOE review before public release.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.** All milestones completed.

4.2 CONTINUOUS TEMPERATURE MONITORING

"The temperature sensors referred to above [Recommendation 90-7.1] should have continuous recorded readouts and alarms that would signal at a permanently manned location any abnormally high temperatures and any failed temperature instrumentation."

This task will provide continuous monitoring of presently installed (and operable) TCs for the ferrocyanide tanks. New TC trees will be connected to the system as they are installed in each tank, resulting in continuous monitoring of all TC trees in the ferrocyanide tanks. All data are collected automatically at the continuously manned Computer Automated Surveillance System (CASS) Operator Control Station. The monitoring system is independent of the CASS and capable of displaying data to an operator on request. Trend data on selected points are available for display in numeric or graphic form.

The system, which became operational in September 1991, has the capacity to assign alarms for a change in the value of any temperature point. Alarms, if they occur, trigger an audible annunciator and are logged immediately to hard copy. An alarm summary display provides a list of the most recent alarms in order of occurrence. Each alarm can be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator.

Signal conditioning and multiplexing are performed locally at each tank. This eliminates the need to transmit low-level signals to the tank farm boundary and reduces cable runs. Electronic noise, extension wire corrosion, and thermal gradients are also reduced.

Five BY Farm tanks were connected to the system in September 1991, and an additional five in December 1991. These tanks include 241-BY-103, -104, -105, -106, -107, -108, -110, -111, and -112. Tank 241-BY-105 has two operating TC trees. Both were connected to the Tank Monitor and Control System (TMACS). In April 1992, tanks 241-TY-101, -103, -104, and 241-TX-118 were connected to the system and are now operational. Four new TC trees installed in tanks 241-BY-104, -110, -111, and -112 have been connected to the TMACS. This makes a total of 13 ferrocyanide tanks (16 TC trees and two LOWs) that are now monitored by the TMACS. Temperature readings from the working TCs in these tanks are being recorded continuously.

- **Progress During Reporting Period.** The design for connection of the tanks in BX Farm is continuing. Designs for all other tank farms are complete. No field work for connection of TMACs occurred this quarter, because of the Administrative Hold placed on work in the tank farms.

- **Planned Work For Subsequent Months.** Work on installation of TMACs in C Farm is anticipated to resume in January 1994.

- **Problem Areas and Action Taken.** Work within the farms is presently restricted because of the Administrative Hold placed on all tank farm work in

August 1993. However, work is slowly resuming as priorities are set and work packages are approved.

- **Milestone Status.**

  - **July 30, 1993:** Complete installation of TMACS for the four ferrocyanide tanks in C Farm. All 12 tanks in C Farm are being connected to TMACS. This task is behind schedule because of the Administrative Hold.

  - **August 30, 1993:** Complete installation of the TMACS for tank 241-T-107. This task is behind schedule because of the Administrative Hold.

  - **September 30, 1993:** Complete design and installation of the TMACS for the two ferrocyanide tanks in the BX Farm. Installation has been delayed because of the Administrative Hold in the tank farms.

  - **September 30, 1993:** Complete installation of the TMACS for new TC trees installed during FY 1993. This milestone has been delayed because of the Administrative Hold.

  - **September 30, 1994:** Complete installation of TMACs for the four C Farm ferrocyanide tanks, one tank in T Farm, and two tanks in BX Farm.

  - **December 31, 1994:** Complete installation of TMACS for new instrument trees installed during FY 1994. In addition, this milestone address the April 1995 TPA milestone M-40-02, upgrade temperature monitoring capabilities in Ferrocyanide tanks.

4.3 COVER GAS MODELING

"Instrumentation should also be installed to monitor the composition of cover gas in the tanks, to establish if flammable gas is present."

4.3.1 Interim Flammable Gas Monitoring

The effort to conduct flammable and toxic gas monitoring and analyses in the ferrocyanide tanks is continuing. Most of this effort was transferred to the Tank Vapor Issue Resolution Program, which is coordinating interim gas monitoring of the ferrocyanide tanks. Tank vapor spaces are measured for flammability using a commercial combustible gas monitor (calibrated with pentane gas), and are monitored for potential toxic gases using an organic vapor monitor and Dräger tubes as required by the safety assessments and work procedures for a particular activity. Development and validation of alternative technologies for vapor space characterization are in progress using Summa canisters and specific absorption tubes. The initial vapor space sampling was done in several tank locations (i.e., from two widely separated risers) and at three elevations in the vapor space. Review of the sample data indicated that sampling from one riser was adequate and the number of sample elevations may be reduced in the future.

To date the vapor space in 11 ferrocyanide tanks have been sampled. In two of the tanks, the combustible gas analyzer reading was reported as one percent of the lower flammability limit (LFL) and all the other ferrocyanide tanks sampled contained <1% of the LFL. The maximum reading for organic vapor was 350 parts per million (ppm), ~0.035 vol%, in tank 241-BY-110, and all other tanks had readings at least an order of magnitude lower. Ammonia has been detected in several of the sampled tanks; the maximum reported value was estimated as 612 ppm, again in tank 241-BY-110. The measured values in the other tanks ranged from <2 ppm to 250 ppm. Hydrogen cyanide measurements with Dräger tube monitoring have all been below 2 ppm (the detection limit for that method). Two tanks, 241-C-108 and -111, have been sampled and analyzed with a more sensitive method and both were reported as less than 0.04 parts per billion (i.e., < 40 parts per trillion). Table A-2 in Appendix A reviews gas analyses for the ferrocyanide tanks sampled to date.

- **Progress During Reporting Period.** No core sampling or instrument tree installation was performed this quarter because of the Administrative Hold. Therefore, there was no need for gas monitoring to support these activities and no additional ferrocyanide tank vapor space samples were taken.

- **Planned Work For Subsequent Months.** Flammable gas sampling and selected noxious gas monitoring will be done, as required, to support planned core sampling and thermocouple tree installation. This work is scheduled to resume next quarter.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status**

  - **September 30, 1995:** Complete vapor space sampling of remaining ferrocyanide tanks to support various field activities. This milestone addresses the November 1995 TPA milestone M-40-03.

4.3.2 Continuous Gas Monitoring

Options for installing a gas monitoring capability on new thermocouple trees have been reviewed and a heated vapor sampling tube has been added to the design of future instrument trees for ferrocyanide tanks (see Section 4.1.1). This will allow vapor space sampling on a continuous or intermittent basis. However, a definitive decision to monitor continuously or just occasionally has not been made. The need for continuous gas monitoring will be addressed in a study that will address the potential for cyclic venting and the possibility of accumulating flammable gases. Evaluation of gas samples secured to date for tanks 241-BY-101, -104, -110, -111, -112; 241-BX-106, -110, -111; 241-C-108, -109, -111, -112; 241-T-101, -107; 241-TX-118 has indicated no need to continuously monitor for specific gases.

The possibility that localized concentrations or stratification of gases exist in the tanks has been evaluated. A modeling effort to determine airflow patterns in the vapor space of tank 241-C-109 was conducted to evaluate the amount of mixing and the local gas concentrations that could occur. The study revealed that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion; therefore, an analysis of a second tank was deemed unnecessary because of the well-mixed environment calculated for 241-C-109 (Wood 1993).

- **Progress During Reporting Period.** A study evaluating potential sources of flammable gases, including potential cyclic venting, was started this quarter. Sampling data is being examined and the report will document the need for continuous vapor space monitoring of selected ferrocyanide tanks.

- **Planned Work For Subsequent Months.** A study to determine the need for continuous monitoring instrumentation will be completed. Continuous gas monitoring will be implemented, on selected tanks, if necessary.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **March 31, 1994:** Complete an evaluation report to determine which gases, if any, need to be continuously monitored on selected ferrocyanide tanks.

  - **September 30, 1995:** Develop and design continuous monitoring equipment (if required).

  - **September 30, 1997:** Install continuous gas monitoring equipment in six tanks (if required).

4.3.3 Tank Pressure Monitoring

The Wyden Amendment (Public Law 101-510) requires that "*...the Secretary of Energy shall identify which single-shell tanks...may have a serious potential for release of high-level waste due to uncontrolled increases of... pressure. After completing such identification, the Secretary shall determine whether continuous monitoring is being carried out to detect a* *release or excessive...pressure at each tank so identified. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring...".*

The ferrocyanide tanks were initially identified as having "a serious potential for release" and were placed on the Watch List; however, pressure monitoring capability does not presently exist for the tanks. It would take several years for the installation of pressure monitoring instrumentation, along with connection to a continuously manned location, because of the capital project time cycle. Sufficient knowledge of the safety of the Ferrocyanide Watch List tanks exists at this time to propose closure of the USQ (see Section 4.0). Because of waste aging, it is possible that all of the ferrocyanide tanks may now contain less than the 8 wt% sodium nickel ferrocyanide specified in the fuel criterion for the SAFE category. It is anticipated that characterization (core sampling and data interpretation) may place all of the tanks into the SAFE category. This would be sufficient to remove them from the Watch List and eliminate the need for continuous pressure monitoring.

- **Progress During Reporting Period.** A study is being conducted that will evaluate the potential for the generation of flammable gases that might cause pressurization of the tank. If the results of this study show that 25 % of the lower flammability limit is not exceeded, a recommendation will be made that no pressure monitoring be installed.

- **Planned Work For Subsequent Months.** Complete study on evaluation of flammable gas generation and the need for continuous pressure monitoring.

- **Milestone Status.**

  - March 30, 1994. Complete studies on the need for continuous flammable gas and pressure monitoring of ferrocyanide tanks.

  - September 30, 1996. Install pressure monitoring for all ferrocyanide tanks (if required).

4.4 FERROCYANIDE WASTE CHARACTERIZATION

"The program of sampling the contents of these tanks should be greatly accelerated. The proposed schedule whereby analysis of two core samples from each single shell tank is to be completed by September 1998 is seriously inadequate in light of the uncertainties as to safety of these tanks. Furthermore, additional samples are required at several radii and at a range of elevations for the tanks containing substantial amounts of ferrocyanide."

Characterization of the waste in the ferrocyanide tanks is necessary to (1) guide further chemical reaction studies with the ferrocyanide waste simulants; (2) determine actual waste chemical and physical properties; (3) determine how the ferrocyanide waste can be safely stored *in situ*, and to classify the tanks accordingly, until retrieval and disposal actions are completed; and (4) apply the study results to the final remediation of the waste in these tanks. Knowledge of the concentration and relative position of various waste constituents is also important for determining the potential for chemical reactions and resulting consequences if a rapid exothermic reaction should occur.

The important reactive materials present in the ferrocyanide tanks are fuel (ferrocyanides, sulfides, and reduced carbon species such as organic complexants), oxidants (nitrates and nitrites), and inerts or diluents (including phosphates, aluminates, sulfates, carbonates, oxides, and hydroxides). The location of fission products such as ^{137}Cs and ^{90}Sr is important because these products are heat sources. Their location is also important because they are potential source terms in postulated radiological releases from a hypothetical ferrocyanide reaction. The water content of the waste is very important because the high heat capacity and the heat of vaporization of water make it an effective inerting material. Water content can prevent a sustained combustion or a propagating reaction. Wet ferrocyanide material would require drying before it could react or propagate.

4.4.1 Core Sampling

The current schedule for ferrocyanide tank sampling will obtain core samples from all ferrocyanide tanks by the end of FY 1995. Both rotary-mode core sampling and push-mode core sampling capability will be available by March 1994 for obtaining core samples from the Watch List tanks. Tanks without saltcake and with relatively soft waste solids can be core sampled by the push-mode method. If a hard saltcake layer is present, rotary-mode core sampling will be used. The first ferrocyanide tank scheduled for rotary-mode core sampling is 241-BY-104 in May 1994.

Each core consists of several 48 cm (19 in.) segments (or portions thereof) depending on the depth of the waste in the tank. The sludge layer in these cores will be divided into four 12 cm (4.75 in.) subsegments for each 48 cm (19 in.) segment. If the tank contains a saltcake layer, the saltcake segments will be divided into only two subsegments. Process flowsheet knowledge, tank historical data, and results obtained from tests with ferrocyanide sludge simulants are used to supplement the analytical results from core sampling.

The priority for sampling ferrocyanide tanks has been changed to reflect the need to determine the reactive properties of the contents. In response to DNFSB Recommendation 93-5 (DOE 1994) to expedite sampling and analyses required to address safety issues in the Hanford Site Watch List tanks, the analysis plans for future ferrocyanide tank core samples (and the plans for other Watch List tanks) have been revised. The Watch List tanks have been given priority for core sampling, and the number of required analytes was reduced and refocused on safety-related properties.

- **Progress During Reporting Period.** A DQO document, *Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process*, WHC-EP-0728 (Buck et al., 1993) was publicly released this quarter. The report provides a statistical basis for the number of cores required to characterize the ferrocyanide tank waste. Based on the distribution of analytes shown in tanks 241-C-109 and -112, the number of cores required to determine the fuel and moisture values for each ferrocyanide tank is two full-depth cores, taken from non-adjacent areas of the tank.

The laboratory data package for tank 241-T-107 was received in late October 1993. Review of the data package and preparation of the data interpretation report was initiated this quarter. Preliminary review of the data identified significant variability among the analyses. The variability can be partially attributed to problems with sample recovery. Sample data that illustrate the variability are shown in Table 4-1.

Table 4-1. Core Sample Analyses of Tank 241-T-107

Core # - Segment#	Sample Recovery (vol%)	Volume of Liquid in Sample (vol%)	Water in Solids (wt%)	Total Cyanide (μg/g)
50-1[a]	34	30	18	49
50-2	94	0	42	64
50-3	96	95	43	43
50-4	67	99	IS	IS
51-1	0	NS	NS	NS
51-2	64	60	60	95
51-3	100	0	54	106
51-4	100	0	52	74
52-1	43	0	17	31
52-2	56	0	49	62
52-3	95	0	53	48
52-4	60	97	59	IS

[a]The designation -1 represents the upper most segment.
IS = Insufficient Sample
NS = No Sample

Only two cores were originally planned for tank 241-T-107, but poor sample recovery from the first core (core 50) made a third core necessary. The percent recovery data of all solids for core 50, segment 2 was good (94%), but pressure in the sampler ejected some material during extrusion causing loss of sample. Segments 3 and 4 were over half full, but the percent liquid and water data indicate that the sample was mostly water and supernatant liquid, not waste solids. Density measurements of the liquid suggests that the water used as hydrostatic head fluid contaminated the sample. Hydrostatic head fluid is used in the push mode core sampler to prevent waste from entering the drill string before the sampler is ready.

Core 51 achieved slightly better results, with complete recovery in the lowermost segments. The first segment of core 51 was empty, but this may have been caused by the uneven surface of the waste. This may also explain the low recovery seen in the first segment of core 50. While the second segment was over half full, it was mostly liquid. The high water content indicates dilution with water from the hydrostatic head fluid.

The first two segments of core 52 recovered only about half of the solid waste that was expected. Recovery for segment 3 of core 52 was all solids, but segment 4 recovered mostly liquid. This liquid is most likely hydrostatic head fluid.

Differential scanning calorimetry analyses of all the quarter segments revealed no exothermic activity except for core 50, segment 4. However, the analyst observed that the only solids recovered in this segment was a small white piece of plastic, which is not representative of the tank waste. This piece of plastic exhibited an exotherm when analyzed. It is believed that only a negligible amount of tank waste sludge was recovered in this segment.

Reconsideration of the discrepancies in the waste analyses will require greater than planned effort and will delay completion of the data interpretation report. The time period to complete the analysis depends on integrated support that is currently being negotiated. Re-sampling of the tank may be necessary, eventually, but this is not a high-priority tank because of its low ferrocyanide inventory.

- **Planned Work For Subsequent Months.** Review of the 241-T-107 sample analysis data will continue and a data interpretation report will be issued. The work to resolve the poor core recovery issue is continuing. Two ferrocyanide tanks are scheduled to be push-mode core sampled in FY 1994; 241-C-108 and -111. It is presently anticipated that push-mode core sampling will resume in March 1994.

Efforts to prepare the rotary-mode core sample system for field are continuing. Rotary-mode is expected to begin in March 1994, and the first ferrocyanide tank scheduled for rotary sampling is 241-BY-104 in May 1994. All core sampling of Watch List tanks is scheduled to be completed by the end of FY 1995.

- **Problem Areas and Actions Taken.** The team formed to examine poor recovery from push-mode core sampling has been dissolved after serving its purpose. Issues are now handled internally by Waste Tank Sampling Engineering. Performance testing and evaluation continues on the redesigned push-mode core sampler. A report on this effort is scheduled to be released next quarter.

- **Milestone Status.**

  - **February 28, 1994**: Complete interpretation of ferrocyanide tank 241-T-107 analytical data and issue a report cleared for public release. This milestone was deferred from September 1993 because core sampling and the laboratory data analysis report were delayed approximately four months.

  - **September 30, 1994**: Two full-length push-mode core samples from three additional ferrocyanide tanks were originally planned in FY 1993. The following order for sampling in the tanks was planned: 241-C-111, -108, and 241-BX-102 (note: tank 241-BX-102 has been recommended for removal from the Watch List). Problems with poor sample recovery and the Tank Farm Administrative Hold have delayed completion of this milestone until FY 1994, and only two tanks (241-C-111 and -108) will be sampled by push-mode.

  - **September 30, 1994**: Secure rotary-core samples from three ferrocyanide tanks (241-BY-104, -106, and -105).

  - **September 30, 1995**: Obtain core samples from the remaining ferrocyanide tanks.

  - **March 31, 1995**: Complete data interpretation reports, available for public release, for five ferrocyanide tanks (241-C-111, -C-108, 241-BY-104, -BY-106, -BY-105). Completion of the reports for the C Farm ferrocyanide tanks should allow Westinghouse Hanford Company to recommend that the Ferrocyanide Safety Issue be resolved for the four C Farm tanks.

  - **August 31, 1995**: Recommend to DOE that the Ferrocyanide Safety Issue is resolved for the four C Farm tanks.

- **February 29, 1996**: Receive DOE approval that the Safety Issue is resolved for the four C Farm ferrocyanide tanks and these tanks can be removed from the Watch List.

- **June 28, 1996**: Complete data interpretation reports, available for public release, for the remaining ferrocyanide tanks.

- **January 31, 1997**: Recommend to DOE that the Safety Issue is resolved for the remaining ferrocyanide tanks.

- **July 31, 1997**: Receive DOE approval that the Ferrocyanide Safety Issue is resolved for the remaining ferrocyanide tanks and these tanks can be removed from the Watch List.

4.4.2 Estimation of Moisture Content

Methods for determining moisture concentrations in ferrocyanide waste tanks are being developed using data analysis and available surveillance systems. Two *in situ* moisture monitoring technologies are currently being pursued by the ferrocyanide program, neutron diffusion and near infrared (NIR) spectroscopy. Additional moisture monitoring technologies, such as copper foil activation, phase change thermal measurement, electrical conductivity, and time domain reflectometry, are being investigated by other programs.

Well-logging techniques, coupled with computer modeling, are being developed and applied to an existing neutron probe to assess this probe and to determine information about moisture levels, material interfaces, and other waste characteristics. The development of a new, improved neutron diffusion based detector system is being investigated. This improved technique would primarily be used to determine the axial moisture concentration profile within the ferrocyanide tanks. The existing neutron probe, used routinely to determine liquid levels, is inserted into closed-bottom LOWs.

Moisture measurement using neutron diffusion is an established technology. The technique uses a neutron source and one or more neutron detectors. The thermal neutrons reaching a detector originate as fast neutrons from the source and are slowed or absorbed by the medium. Because hydrogen atoms are effective at slowing down neutrons, the detector response is a strong function of the surrounding moisture concentration.

Two methods are generally used in the measurement of moisture concentration around wells using neutron diffusion. The first method, the moisture gauge, has a short source-to-detector spacing on the order of 0 (the source is placed in a ring around the detector) to 6 cm. The response of a moisture gauge is characterized by an increase in detector response with increasing moisture concentration of the surrounding medium. The second method, the neutron log, often has two detectors with longer source-to-detector spacings (20 to 50 cm). The detectors in a neutron log arrangement exhibit a decreased response to increased moisture concentrations. The detector placed at the shorter spacing is used to correct the response of the longer spaced detector for borehole effects.

The source-to-detector spacing of the existing probe may be adjusted with the addition of a source extender. Computer modeling of the existing neutron probe system revealed that, in its current configuration, it responds most like a moisture gauge. The probe will operate as a neutron log with the addition of a source extender.

- **Progress During Reporting Period.**

Neutron Diffusion. Using the knowledge gained from both computer modeling and *in situ* and experimental measurements with the current in-tank neutron probe (Watson 1993), prototype moisture measurement neutron probes have been designed and are being assembled. These prototype devices will utilize both thermal and epithermal neutron detectors, and will allow for both shorter and longer source-to-detector spacings than the current in-tank probe. In order to test and evaluate the prototype probes, a test area is being set up.

The effects of annular air gaps around LOWs on moisture sensitivity continues to be examined. Studies have included modeling and visualization of the interrogation of the probe as it scans through material interfaces surrounding an LOW. These studies are leading to an increased understanding of the moisture interpretation of scans obtained from several ferrocyanide tanks.

A study was performed to investigate the feasibility of designing a miniature moisture measurement neutron probe for deployment inside a small diameter well, such as a penetrometer. The study demonstrated that a limited size probe can be readily designed for deployment in a penetrometer to measure moisture concentrations in waste tanks not equipped with LOWs. The analyses were performed for a well with a nominal inside diameter of 1.25 inches; however, the probe configuration could be adjusted for other geometries. The results of this study could also be used to develop a smaller neutron probe to fit within relined LOWs. The primary technical concern associated with this type of probe is the feasibility of developing a small detector configuration that (1) exhibits good neutron sensitivity for obtaining an accurate moisture measurement; (2) but is not sensitive to the high gamma flux environment in the waste tanks.

Results of preliminary computer modeling showed that it is feasible to develop a smaller size neutron probe with the desired characteristics of high moisture sensitivity and sufficient gamma discrimination. To match the moisture measurement accuracy of the existing in-tank neutron probe, the length of counting time would most likely have to be increased. Approximately 30 - 60 minutes may be needed to scan 10 feet of tank waste.

A modeling study has been completed to compare and assess the impact of LOW material type and wall thickness on the expected moisture measurement sensitivity of the prototype probes (Toffer 1993). The three most important factors to consider in the selection of LOW material for a neutron moisture probe are (1) effects on the moisture sensitivity; (2) expected detector count rate; and (3) depth of interrogation into the waste. The comparisons were made for LOWs of identical thickness. This study showed that the LOW material type has little impact on these factors for an epithermal neutron detector probe. However, for a thermal neutron detector probe, the LOW material type is expected to have a significant impact on the moisture measurement sensitivity, the count rate, and the range of interrogation of the probe.

Figure 4-2 shows the predicted response of the current in-tank neutron probe to increasing moisture concentration for several LOW materials. The predicted probe responses for all modeled LOW materials are significantly higher than for the current borosilicate fiberglass LOWs. Higher counting rates enable quality data to be obtained in shorter time intervals. Figure 4-3 shows the results of Figure 4-2 with the changing detector responses normalized to show fractional increase in the response with increasing moisture concentration. The slope of this normalized fractional increase is equivalent to the sensitivity of the probe response to changes in surrounding moisture concentration. The LOW materials corresponding to steepest curves in this plot would provide the greatest moisture sensitivity to a thermal neutron probe. Among the modeled materials, the best sensitivity would be obtained using aluminum or zirconium; however, aluminum would not be compatible with the caustic environment in the tanks.

The radial depth of interrogation expected for the current in-tank neutron probe into 30 wt% moisture sludge varies slightly with LOW material. The approximate depth of investigation for the probe ranges from about 40.5 cm for a steel LOW to about 44 cm for a TEFZEL[2] LOW. For the same thickness LOW, the plastic and epoxy-based LOWs should allow for a slightly increased range of interrogation over metal LOWs.

The thickness of the LOW affects the probe response in a predictable manner. Increasing the LOW thickness for all materials decreases the probe sensitivity to changing moisture concentration. For metal LOWs, the detector count rate is expected to increase with decreasing LOW thickness. For the plastic and epoxy LOWs, the detector count rate is expected to slightly decrease with decreasing LOW thickness. The hydrogen content of the plastic or epoxy LOWs acts to increase the baseline count rate for a moisture gauge thermal probe.

[2]Trademark of E. I. duPont de Nemours & Company

Figure 4-2. Model Predicted Detector Response to Increasing Moisture Concentration Sludge for Several LOW Materials.

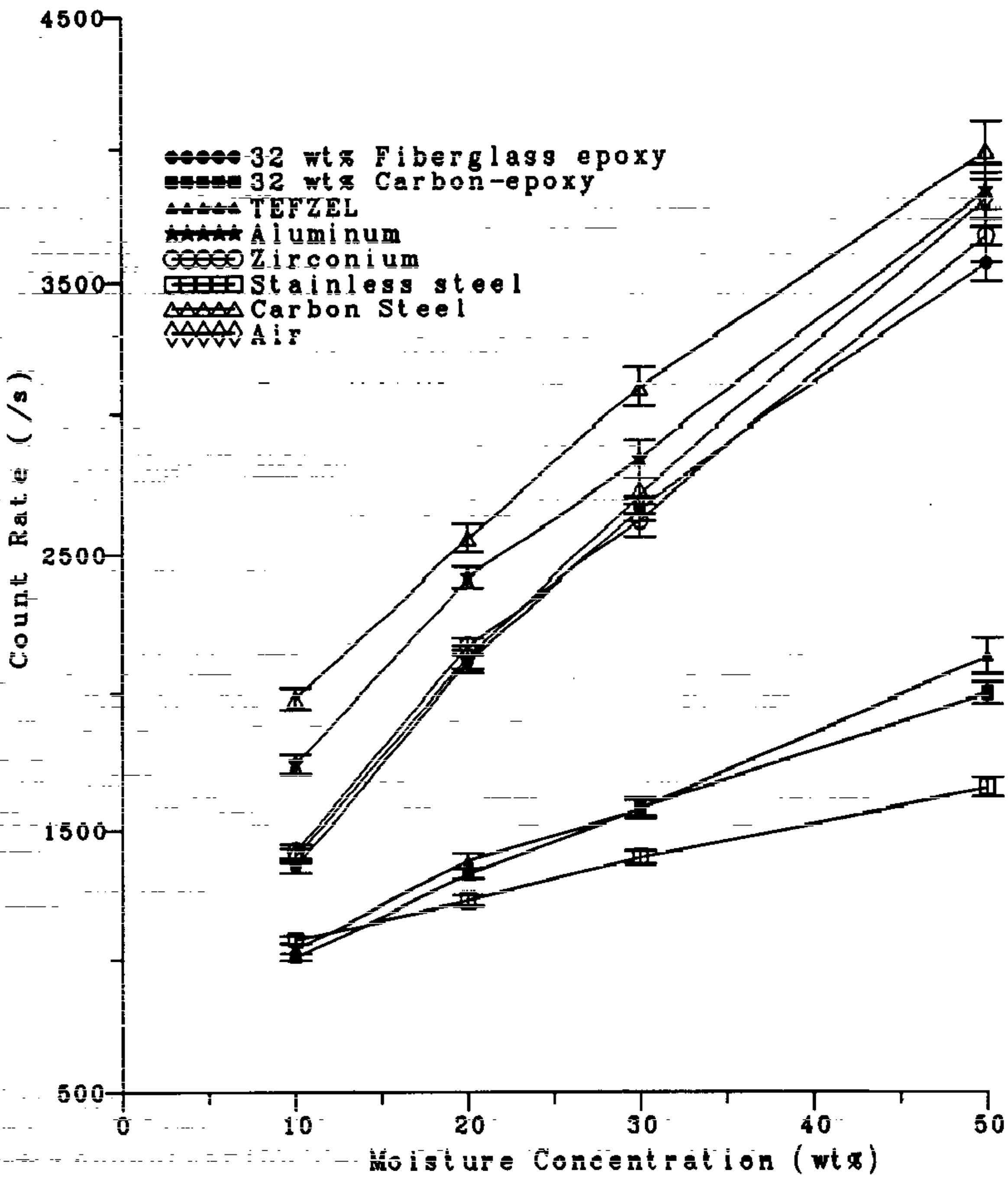
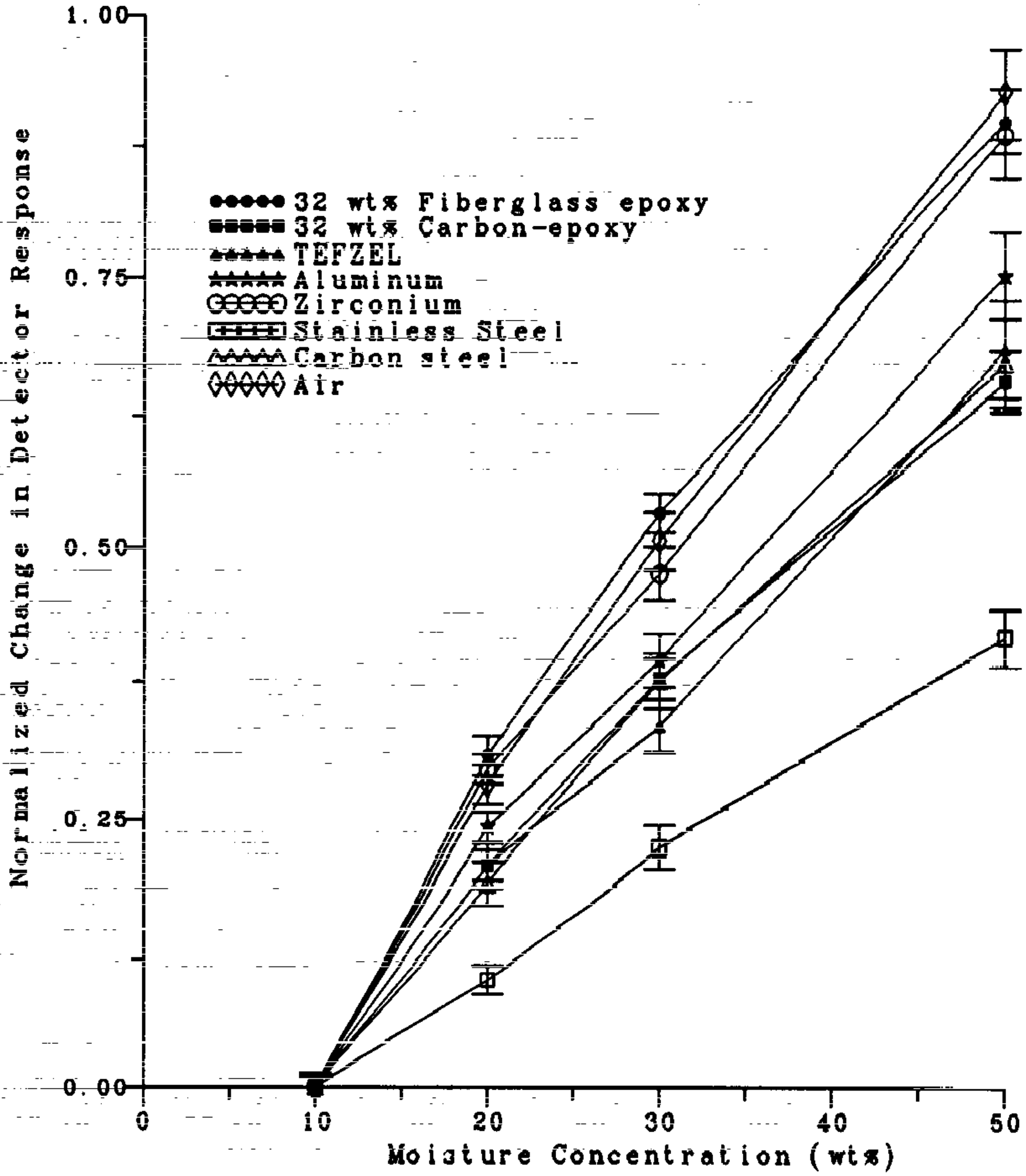


Figure 4-3. The Predicted Fractional Increase in Detector Response to Increasing Moisture Concentration for Several LOW Materials.



Near Infrared Spectroscopy. The University of Washington's Center for Process Analytical Chemistry (CPAC) has completed a Phase 1 study of the feasibility of measuring saltcake surface moisture with optical scattering techniques (Veltkamp 1993). Comparison studies for three spectral regions (visible, NIR, and mid-infrared) on a 241-BY-104 saltcake simulant, indicated that the NIR region produced the best moisture sensitivity and the simplest (one parameter) calibration model. Over a range of 0 to 20 wt% moisture, the NIR calibration model predicted water within a 0.5 wt% limit. Issues such as particulate size and material matrix changes, are being explored in the Phase 2 work. The Phase 2 work also includes a full-scale demonstration experiment that indicates feasibility at tank scale dimensions for non-contact sensing.

A spectrometer system with a fiber optic probe is being delivered to Westinghouse Hanford by Savannah River Laboratory (SRL). The plan is to integrate the CPAC NIR calibration model with this system for a remote probe moisture sensing system. Non-radioactive (cold) materials will be used to feature test this system. The remote fiber optic probe system has potential application in hot cells and with *in situ* waste tank penetrometer systems.

- **Planned Work for Subsequent Months.** An experimental test area in which to complete the final development, testing, and calibration of a prototype neutron diffusion-based moisture measurement system will be set up. This laboratory will allow necessary controlled experimental measurements to be made as desired.

  A two or three detector neutron probe will be modeled to determine if a pulsed neutron source can delineate additional information about the surrounding medium. The identification of, and compensation for, air or liquid-filled space immediately surrounding the LOW will be explored. The use of an epithermal neutron detector to eliminate any effects on detector response from the presence of unknown amounts of strong neutron absorbers in the tank waste will be examined. Testing to determine the response of probes to material interfaces will be pursued. A simulant more representative of the neutronic properties of ferrocyanide waste will be identified and used to obtain probe data as a final check for the Monte Carlo Neutron Photon (MCNP) model.

  The integration of a SRL NIR system with the CPAC calibration model will be initiated and materials for cold feature testing will be identified. A report on CPAC Phase 2 moisture sensing feasibility work will be published and Phase 3 work scope optimizing the calibration model will be completed.

- **Problem Areas and Action Taken.** Simulants, neutronically equivalent to ferrocyanide waste, with known moisture (hydrogen) concentrations must be acquired for final testing and calibration. In order to correct for material inhomogeneities around the LOW, experimental results will be needed in simulants arranged to model anticipated material geometries. These results will be used to confirm modeling results for a few selected physical situations and moisture contents. Potential simulant compounds containing elements expected to be present in tank waste have been identified and their neutronic properties are being modeled in order to find suitable moisture waste simulants.

The apparent observed effects of nonuniform LOW boron concentrations has led to the conclusion that the use of one or more epithermal detectors should be pursued. This should eliminate the measurement uncertainty from this factor.

- **Milestone Status.**

  - **April 30, 1993:** Evaluate moisture monitoring technology suitable for *in situ* moisture measurement. A report, *Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools* (WHC-EP-0658), was publicly released in April 1993 (Meacham et al., 1993b).

  - **September 27, 1993:** A comprehensive neutron probe moisture measurement proof of principle letter report was completed on schedule. The report was subsequently released as a publicly available report in December 1993 (Watson 1993).

  - **December 31, 1993:** A riser survey for insertion of new LOWs into ferrocyanide Watch List tanks was completed and a report assessing the effects of LOW material on the sensitivity of a neutron moisture probe was issued on schedule (Toffer 1993).

  - **September 30, 1994:** Provide a working prototype neutron probe system for moisture monitoring with documentation.

  - **September 30, 1994:** Complete review and design of dry well van modifications as required.

  - **September 30, 1995:** Complete first phase of neutron moisture monitoring installation and initiate monitoring.

  - **September 30, 1996:** Complete installation of neutron moisture monitoring equipment.

  - **February 25, 1994:** Complete the phase 2 surface monitoring interference study/scale up report.

  - **September 30, 1994:** Initiate a phase 3 surface monitoring contract and provide a report.

- **September 30, 1995:** Complete surface moisture measuring development work and in-tank demonstration.

- **September 30, 1996:** Initiate installation of surface moisture monitoring equipment if demonstration is successful and if the need is warranted.

- **September 30, 1997:** Complete installation of surface moisture monitoring system.

4.4.3 Preparation and Characterization of Ferrocyanide Waste Simulants

Ferrocyanide waste precipitates are being prepared and analyzed to determine the composition, physical properties, and chemical reaction properties of simulants that represent ferrocyanide waste stored in SSTs. The analytical results from these simulants, along with analyses of actual tank waste samples, waste tank monitoring, and waste modeling, provide information to characterize any safety concerns of the sludge in each of the ferrocyanide tanks with a great deal of assurance. The results will also provide a technical basis for (1) safety measures to be taken; (2) decisions on appropriate actions leading to closure of the Ferrocyanide USQ; and (3) eventual resolution of the Ferrocyanide Safety Issue.

Five waste simulants (without radioactive species) are being used to represent the variety of waste produced in the mid-1950s and stored in SSTs. The wastes produced at the Hanford U Plant are represented by U Plant 1 and U Plant 2 test mixtures. The U Plant 1 waste simulant represents 41 of 59 batches and the U Plant 2 simulant represents 9 of 59 batches of U Plant waste. The average U Plant batch volume was about 2,300,000 L (600,000 gal). The other nine batches of U Plant waste are expected to have a ferrocyanide concentration between that of U Plant 1 and U Plant 2. A test mixture representing these batches will not be prepared and tested.

The In Farm flowsheet waste (in four C Farm tanks) is represented by In Farm 1 and In Farm 2 test mixtures. The In Farm 1 test mixture is representative of one batch (expected to have the greatest ferrocyanide concentration) of the 29 in farm batches processed in the 1950s. In Farm 2 is representative of 11 intermediate ferrocyanide concentration batches of the 29 in farm batches. An average size In Farm batch was approximately 1,500,000 L (400,000 gal). It should also be noted that six of these 29 scavenging batches did not contain any ferrocyanide, but sodium sulfide was added to enhance precipitation of ^{60}Co.

A T Plant simulant was prepared for testing to represent the six T Plant batches produced. An average sized T Plant batch was 2,098,000 L (554,000 gal). The T Plant ferrocyanide sludge is stored in three TY Farm tanks.

Three main adjustments from the actual processes used in the 1950s were made in the laboratory scavenging preparation method to provide waste simulants representative of ferrocyanide sludges. These changes are as follows: (1) the solution concentrations were adjusted to include nitrite at a 1:3 mole ratio of nitrite/nitrate, to account for nitrite buildup over time in the wastes by radiolysis of nitrate; (2) the waste simulants prepared for characterization do not contain radioactive isotopes present in actual waste, because of the difficulty in working with radioactive materials; and (3) the settled waste simulants from the laboratory scavenging process were centrifuged at a force of ~2,500 gravities (g) to mimic an equivalent 30 year settling period.

The moisture content of ferrocyanide sludge is very important in the exothermic reaction behavior of ferrocyanide/nitrate-nitrite mixtures when ferrocyanide is present at concentrations greater than 8 wt% disodium mononickel ferrocyanide. Studies are underway to evaluate the moisture retention properties of ferrocyanide simulants to relate to possible waste tank leaks, tank stabilization by pumping, and possible evaporation from exposed surfaces.

- **Progress During Reporting Period.** The ferrocyanide content of the T Plant simulant fractions and supernatant were determined. A summary of chemical compositions of dried ferrocyanide waste simulants (U Plant, T Plant, and In Farm) is presented in Table 4-2. Moisture drainage, retention, and evaporation behavior tests were continued to evaluate possible end-point water content of simulants for postulated tank leaks, stabilization, or evaporation.

  Dried T Plant simulant contained a stoichiometric excess of nitrate/nitrite and 0.8 wt% total cyanide in the bottom fraction and 4.4 wt% total cyanide in the top fraction. The fuel in the T Plant simulant is much less concentrated than in the In Farm simulants. The cesium content of the scavenged supernatant was less than 0.1 ppm.

Table 4-2. Analyses of U Plant, T Plant, and In Farm Ferrocyanide Simulants

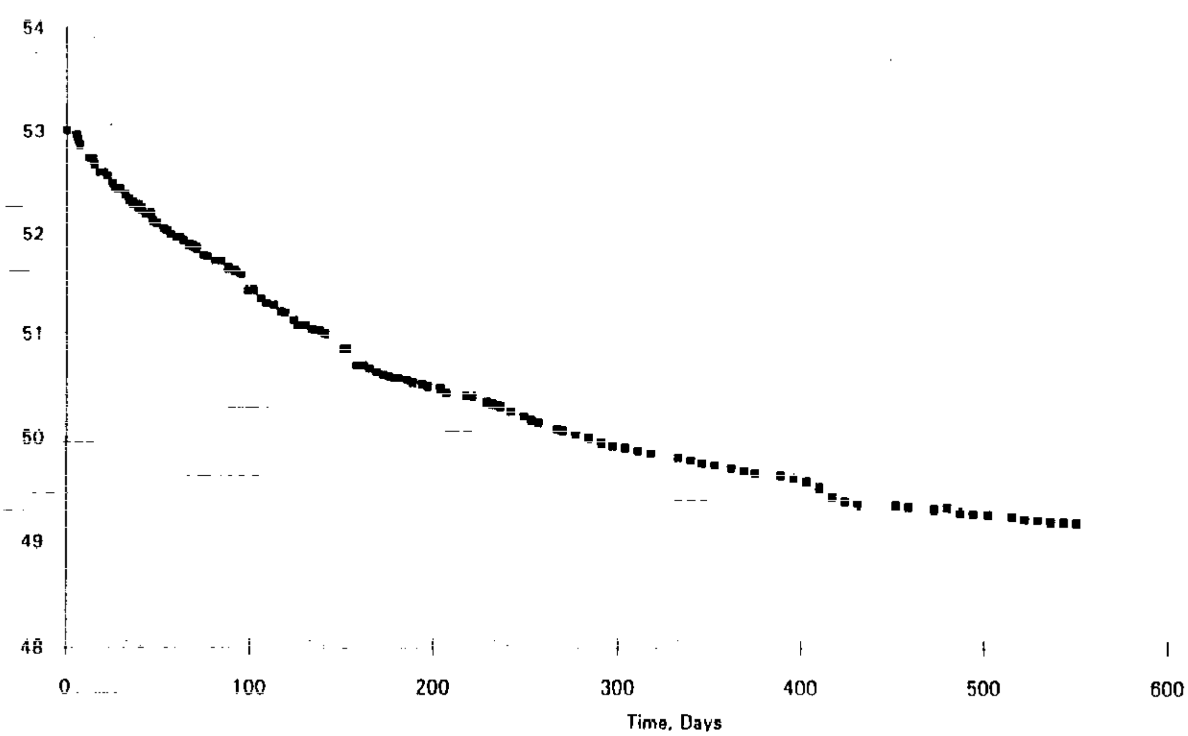
Constituent	Dried U Plant 2 bottom fraction	Dried In Farm 1 bottom fraction	Dried T Plant top fraction
	Weight Percent		
Bound Water	2.5	5.4	3
Nitrate	33.0	29.0	19.8
Nitrite	7.7	8.1	4.3
$Na_2NiFe(CN)_6$*	8.3	25.6	8.8
Nickel Sulfide	0.0	2.7	0.0
Inert Solids	~33	~15	~55

*Assuming all measured ferrocyanide is disodium mononickel ferrocyanide.

Tests are continuing to determine the amount of moisture remaining in the simulants in the event of a free flowing drainage, such as a tank leak or saltwell pumping of liquids for tank stabilization. Three types of tests have been or are being conducted: (1) a free flowing liquid drainage test using In Farm 2 top fraction simulant at one atmosphere pressure; (2) centrifuge tests with open ended drainage at gravity forces up to 100 g on In Farm simulant; and (3) gas pressure tests on In Farm simulant loaded in Tempe[3] cells.

The free flowing liquid drainage test has continued 18 months. A 4 inch diameter column was filled to a height of 8 inches with In Farm simulant and allowed to gravity drain. The initial free water content of the simulant was 53 wt%. Calculations from the measured liquid drained to date indicate that the remaining material has a water content of about 47 wt% (Figure 4-4). Liquid is continuing to drain very slowly from this material with no apparent termination anticipated in the near future. Some consolidation of this simulant has been observed during the test.

Figure 4-4. Weight Percent of Free Water Remaining as a Function of Time.



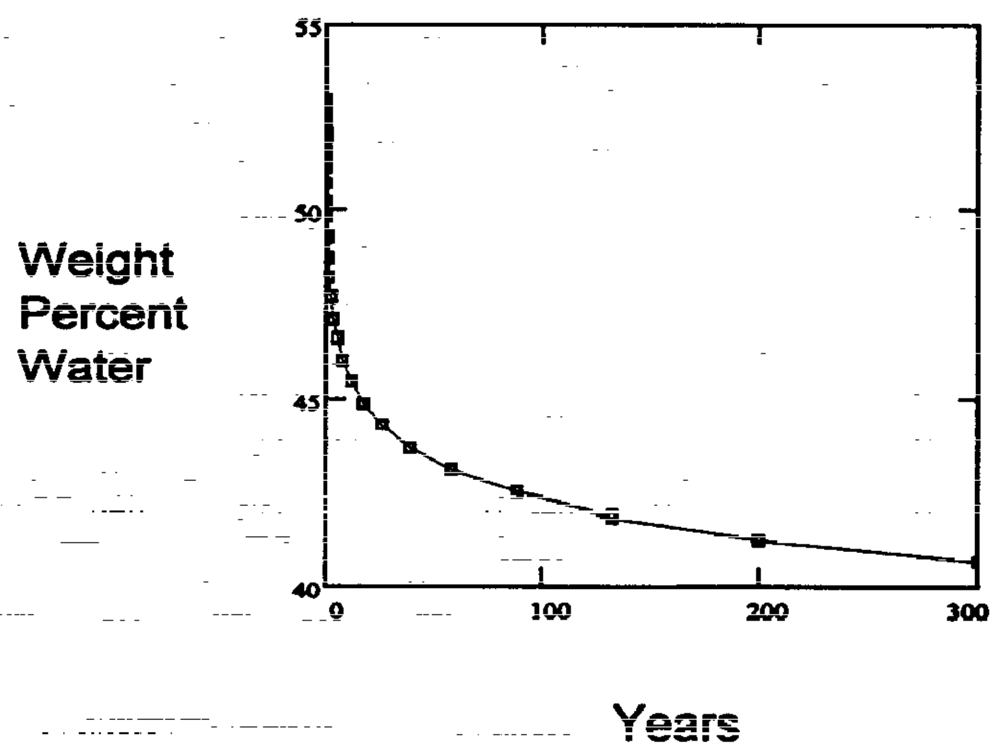
[3]Trademark of Soil Moisture Equipment Corporation, Santa Barbara, California.

Scoping, vented centrifugation tests conducted at 10, 20, 50, and 100 g centrifugal force with In Farm simulant on a fritted porus media (30 μm sized openings) resulted in final water contents of about 48, 47, 46, and 45 wt%, respectively. This identifies a final water content which is above the minimum water required to prevent propagation of the most concentrated ferrocyanide simulant. Consolidation was observed but not measured in these tests.

Moisture retention tests using gas pressures on loaded Tempe cells have been conducted for pressures at 10, 15, 100, 200, 300, and 500 cm of water. Consolidation of simulant was observed and repacking of the simulant was performed as needed. The point of air entrainment has not been reached at these pressures but additional testing is underway at higher pressures.

Modeling analysis of simulant drainage is continuing to evaluate ferrocyanide sludge water loss if allowed to gravity drain. The model simulates flow of a highly concentrated solution of nitrate salts through an unsaturated porous medium. Data from the small column, centrifugation experiments, and Tempe cell tests are being used to estimate the hydraulic properties that control liquid flow in the sludge. Figure 4-5 shows water remaining as a function of time for an 8 feet deep sludge layer. The model indicated that the sludge would still contain 40 wt% water even after 200 to 300 years of drainage.

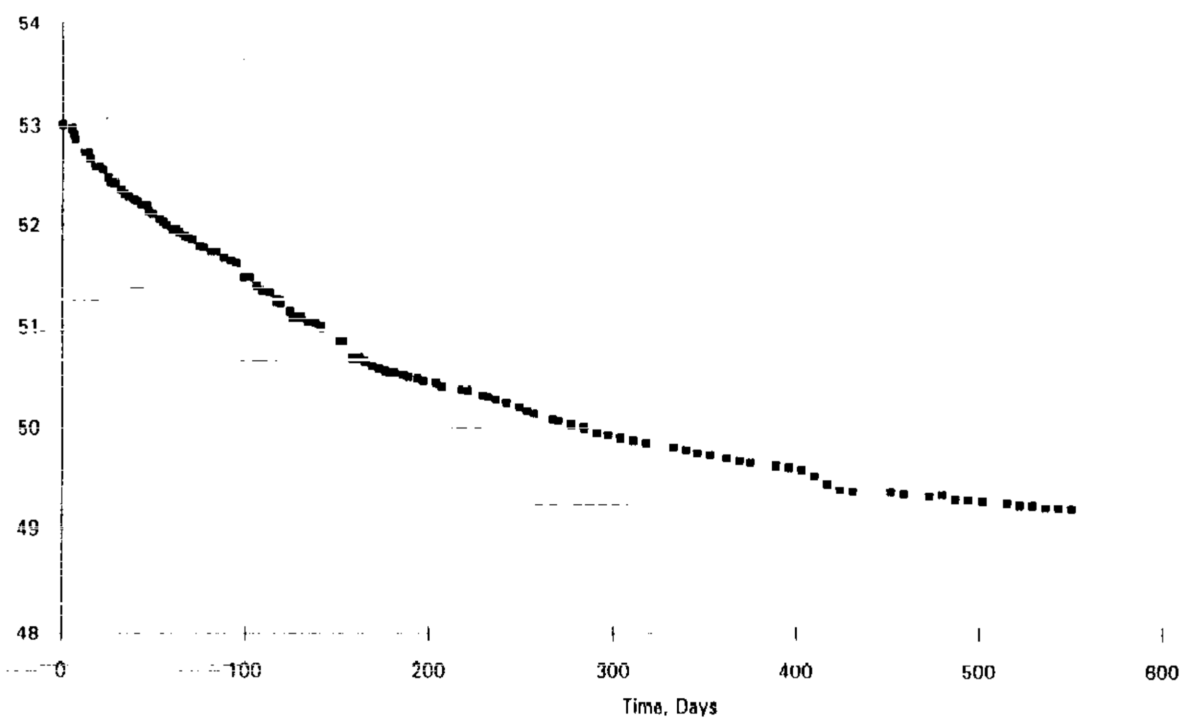
Figure 4-5. Water Concentration at the Surface of an Eight Foot Column of Ferrocyanide Sludge as a Function of Drainage Time.



Tests are continuing to determine the amount of moisture remaining in the simulants in the event of a free flowing drainage, such as a tank leak or saltwell pumping of liquids for tank stabilization. Three types of tests have been or are being conducted: (1) a free flowing liquid drainage test using In Farm 2 top fraction simulant at one atmosphere pressure; (2) centrifuge tests with open ended drainage at gravity forces up to 100 g on In Farm simulant; and (3) gas pressure tests on In Farm simulant loaded in Tempe[3] cells.

The free flowing liquid drainage test has continued 18 months. A 4 inch diameter column was filled to a height of 8 inches with In Farm simulant and allowed to gravity drain. The initial free water content of the simulant was 53 wt%. Calculations from the measured liquid drained to date indicate that the remaining material has a water content of about 47 wt% (Figure 4-4). Liquid is continuing to drain very slowly from this material with no apparent termination anticipated in the near future. Some consolidation of this simulant has been observed during the test.

Figure 4-4. Weight Percent of Free Water Remaining as a Function of Time.



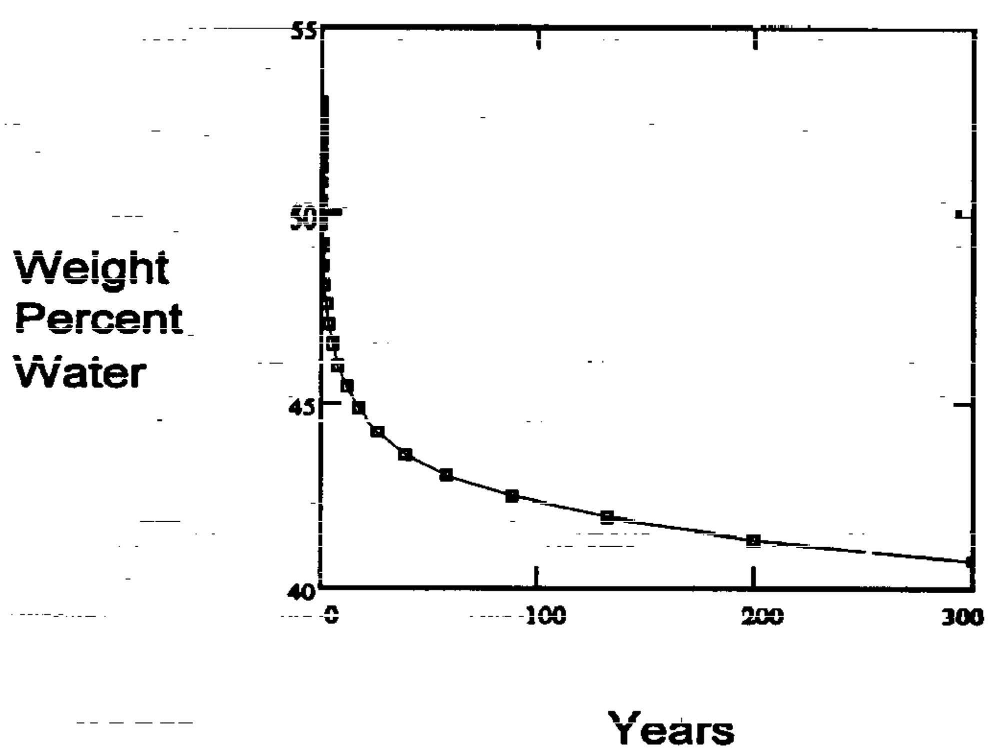
[3]Trademark of Soil Moisture Equipment Corporation, Santa Barbara, California.

Scoping, vented centrifugation tests conducted at 10, 20, 50, and 100 g centrifugal force with In-Farm simulant on a fritted porus media (30 μm sized openings) resulted in final water contents of about 48, 47, 46, and 45 wt%, respectively. This identifies a final water content which is above the minimum water required to prevent propagation of the most concentrated ferrocyanide simulant. Consolidation was observed but not measured in these tests.

Moisture retention tests using gas pressures on loaded Tempe cells have been conducted for pressures at 10, 15, 100, 200, 300, and 500 cm of water. Consolidation of simulant was observed and repacking of the simulant was performed as needed. The point of air entrainment has not been reached at these pressures but additional testing is underway at higher pressures.

Modeling analysis of simulant drainage is continuing to evaluate ferrocyanide sludge water loss if allowed to gravity drain. The model simulates flow of a highly-concentrated solution of nitrate salts through an unsaturated porous medium. Data from the small column, centrifugation experiments, and Tempe cell tests are being used to estimate the hydraulic properties that control liquid flow in the sludge. Figure 4-5 shows water remaining as a function of time for an 8 feet deep sludge layer. The model indicated that the sludge would still contain 40 wt% water even after 200 to 300 years of drainage.

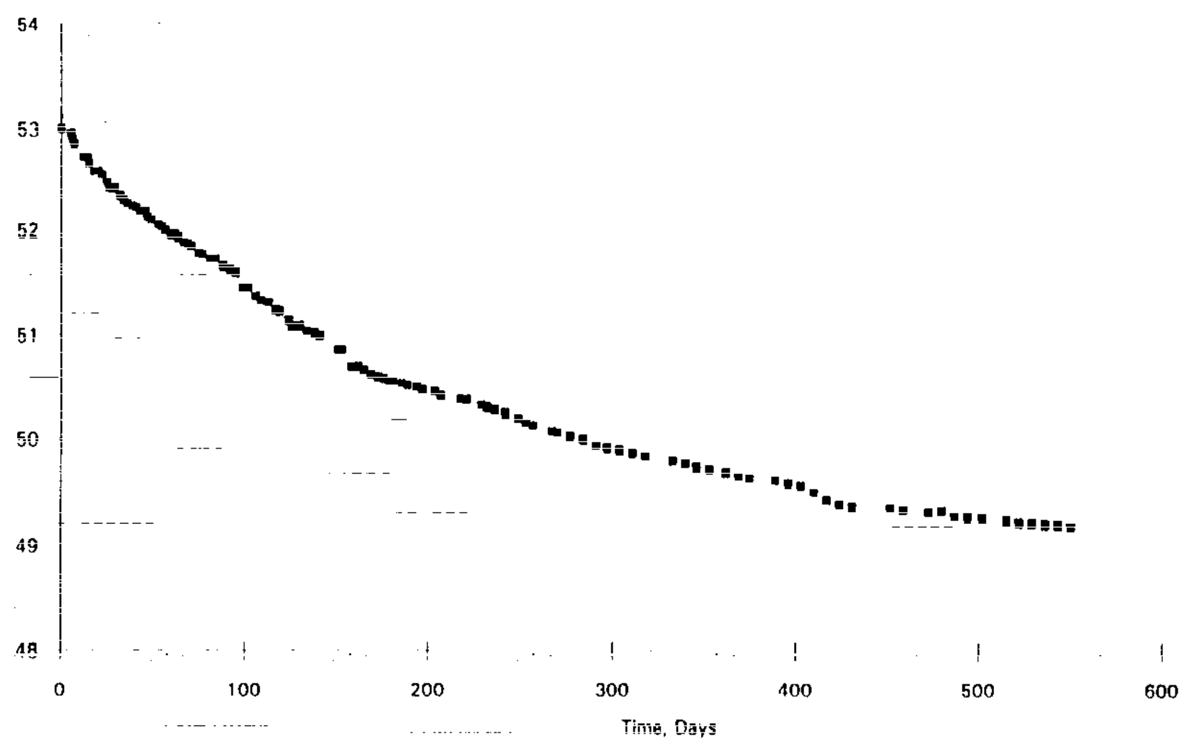
Figure 4-5. Water Concentration at the Surface of an Eight Foot Column of Ferrocyanide Sludge as a Function of Drainage Time.



Tests are continuing to determine the amount of moisture remaining in the simulants in the event of a free flowing drainage, such as a tank leak or saltwell pumping of liquids for tank stabilization. Three types of tests have been or are being conducted: (1) a free flowing liquid drainage test using In Farm 2 top fraction simulant at one atmosphere pressure; (2) centrifuge tests with open ended drainage at gravity forces up to 100 g on In Farm simulant; and (3) gas pressure tests on In Farm simulant loaded in Tempe[3] cells.

The free flowing liquid drainage test has continued 18 months. A 4 inch diameter column was filled to a height of 8 inches with In Farm simulant and allowed to gravity drain. The initial free water content of the simulant was 53 wt%. Calculations from the measured liquid drained to date indicate that the remaining material has a water content of about 47 wt% (Figure 4-4). Liquid is continuing to drain very slowly from this material with no apparent termination anticipated in the near future. Some consolidation of this simulant has been observed during the test.

Figure 4-4. Weight Percent of Free Water Remaining as a Function of Time.



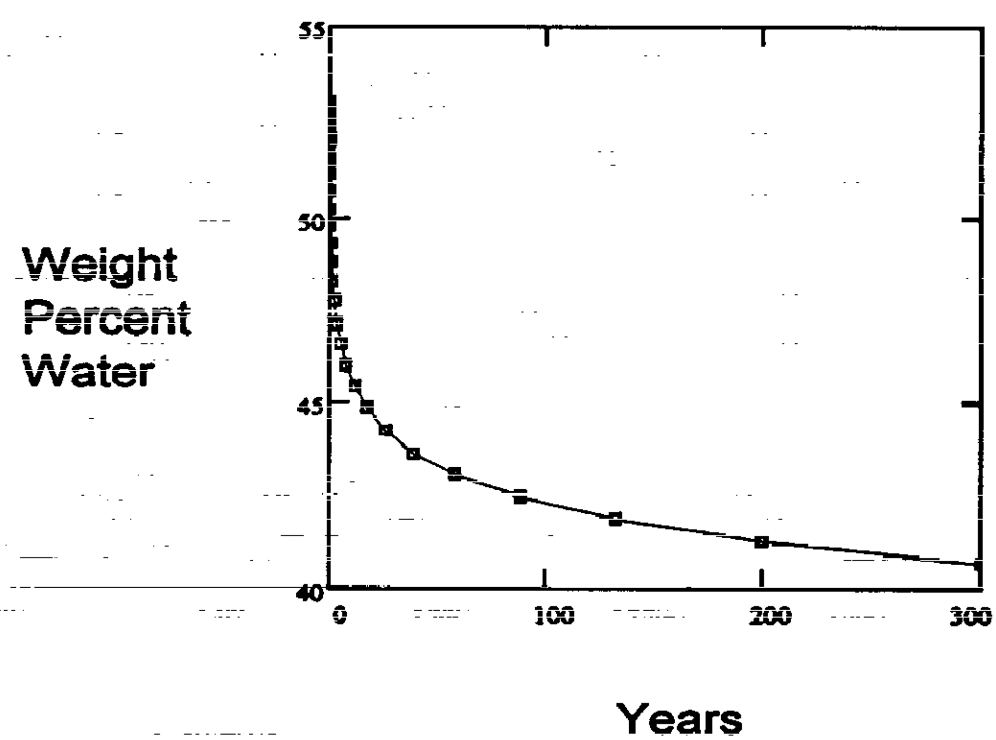
[3]Trademark of Soil Moisture Equipment Corporation, Santa Barbara, California.

Scoping, vented centrifugation tests conducted at 10, 20, 50, and 100 g centrifugal force with In Farm simulant on a fritted porus media (30 μm sized openings) resulted in final water contents of about 48, 47, 46, and 45 wt%, respectively. This identifies a final water content which is above the minimum water required to prevent propagation of the most concentrated ferrocyanide simulant. Consolidation was observed but not measured in these tests.

Moisture retention tests using gas pressures on loaded Tempe cells have been conducted for pressures at 10, 15, 100, 200, 300, and 500 cm of water. Consolidation of simulant was observed and repacking of the simulant was performed as needed. The point of air entrainment has not been reached at these pressures but additional testing is underway at higher pressures.

Modeling analysis of simulant drainage is continuing to evaluate ferrocyanide sludge water loss if allowed to gravity drain. The model simulates flow of a highly concentrated solution of nitrate salts through an unsaturated porous medium. Data from the small column, centrifugation experiments, and Tempe cell tests are being used to estimate the hydraulic properties that control liquid flow in the sludge. Figure 4-5 shows water remaining as a function of time for an 8 feet deep sludge layer. The model indicated that the sludge would still contain 40 wt% water even after 200 to 300 years of drainage.

Figure 4-5. Water Concentration at the Surface of an Eight Foot Column of Ferrocyanide Sludge as a Function of Drainage Time.



The modeling results are still tentative because consolidation processes and possible evaporative loss of water were not included. The present unsaturated flow analysis presumes that the sludge matrix remains rigid. Moreover, sludge would dry out at the surface if exposed to sufficiently low relative humidity gases. This modeling study did not consider evaporation at the surface if relative humidity is less than saturation.

Free water adsorption/desorption experiments were performed by Nuclear Consulting Services Inc. on In Farm 2 top fraction simulant (see also Appendix C in Postma et al., 1993). About 1 g quantities of simulant (containing an initial 53 wt% water) were exposed in controlled humidity chambers to 30%, 50%, 75%, and 90% relative humidities at 25 ± 1°C. The simulant samples exposed at 30%, 50%, and 75% relative humidity (RH) all lost weight. The simulants retained 4.1 wt%, 10.6 wt%, 31.3 wt%, and 65.4 wt% free water, respectively, at equilibrium, respectively, within a 96 hour time period. The simulant exposed to 90% RH gained 36.0 wt% water at equilibrium after approximately 216 hours.

Additional adsorption/desorption tests were conducted with the test material exposed to the 30% RH and 90% RH atmospheres by re-exposing them to 90% and 30% RH atmospheres, respectively. Cumulative weight changes were +36.1 wt% of the original sample for re-exposure to 90% RH after 220 hours and -51.2 wt% of the original sample for re-exposure to 30 wt% RH after 48 hours.

These test results indicate that the equilibrium water content of the simulant is strongly dependent on the relative humidity of the exposed atmosphere. The following equation was derived from the sample results to express the equilibrium water adsorption isotherm of the simulant on a dry weight basis (oven drying at 120°C for 18 hours) as a function of relative humidity:

$$\log(\text{wt\% water adsorbed}) = 0.02218(\%\text{RH}) - 0.03246$$

Much of the ferrocyanide sludge stored in the tanks is covered with a saltcake layer or has a liquid level above the sludge level with the possible exceptions of four interim stabilized tanks: 241-C-108, -C-111, -TY-101, and -TY-103. Humidity in these tanks may be measured at a later date.

- **Planned Work for Subsequent Months**. A ferrocyanide waste simulant based on characterization of actual tank waste samples will be prepared, analyzed, and tested. Simulant drainage and centrifugation tests will continue. The effects of relative humidity in air on the loss and absorption of moisture will be evaluated under geometric conditions representative of the SSTs.

A test report on the results of the centrifuge tests will be prepared for public release.

A report on the three methods used for drying the ferrocyanide waste simulants will be prepared and issued.

- **Problem Areas and Actions Taken.** None

- **Milestone Status.**

  - **March 31, 1994:** Issue a report, available to the public, on the evaluation of the three waste simulant drying methods.

  - **March 31, 1994:** Issue a report, available to the public, on the effect of centrifugation on water retention by the In Farm simulant.

  - **May 31, 1994:** Issue a report, available to the public, on the chemical and physical properties of the T Plant ferrocyanide waste simulant.

  - **September 30, 1994:** Complete drainage tests on ferrocyanide waste simulants and issue a publicly available report on modeling and moisture retention by ferrocyanide sludge.

  - **September 30, 1994:** Issue a publicly available report on the effects of relative humidity on surface moisture retention in ferrocyanide tanks.

4.5 CHEMICAL REACTION STUDIES

"The schedule for the program on study of the chemical properties and explosive behavior of the waste in these tanks is indefinite and does not reflect the urgent need for a comprehensive and definitive assessment of the probability of a violent chemical reaction. The study should be extended to other metallic compounds of ferrocyanide that are known or believed to be present in the tanks, so that conclusions can be generalized as to the range of temperature and other properties needed for a rapid chemical reaction with sodium nitrate."

Chemical reaction studies on ferrocyanide waste simulants are being conducted by Westinghouse Hanford Company, FAI, PNL, Los Alamos National Laboratory (LANL), and Washington State University. Westinghouse Hanford Company and PNL have produced flowsheet simulant materials for testing and characterization. In FY 1992, LANL completed chemical reaction sensitivity tests on ferrocyanide waste simulants to identify what stimuli (emphasizing non-thermal) may cause a reaction to occur (Cady 1993). FAI is conducting adiabatic calorimetry and propagation tests on these same replicated flowsheet materials. The FAI scope of work was expanded in FY 1993 to include selected aerosol studies.

4.5.1 Chemical Reaction Studies at Pacific Northwest Laboratory

Chemical reaction studies are continuing at PNL using flowsheet simulant materials. Waste studies addressing DNFSB Recommendation 90-7.5 were conducted to determine (1) the aging effects of more than 35 years of storage in the tanks; (2) the speciation of cyanides found in actual tank waste; (3) possible microconvection mechanisms that may have allowed mixing of the ferrocyanide sludge with caustic solutions added to the tanks at a later time; (4) the influence of chemical interactions and physical changes on the solubility of sodium and cesium nickel ferrocyanides; and (5) the reaction kinetics of mixtures of sodium nickel ferrocyanide and sodium nitrate/nitrite.

- **Progress During Reporting Period.**

Aging Studies. Ferrocyanide dissolution and hydrolysis screening studies were continued during the quarter with experiments conducted at pH 10 and 60°C to investigate the behavior of ferrocyanide materials that may not have been exposed to high pH waste. A sample of dried In Farm 1 simulant was contacted with a pH 10 carbonate buffer solution for four weeks at 60°C in a gamma field of 1.43×10^5 Rad/h. Sodium concentration in the solution was adjusted to 1 *M* with $NaNO_3$. An identical reaction mixture was heated to 60°C outside the gamma field as a control. Ammonia concentrations observed in this experiment, for both the control and irradiated solutions, were two orders of magnitude less than those observed in a previous hydrolysis experiment conducted in 4 *M* NaOH. The formate concentrations measured by ion chromatography (IC) were also much lower in the solutions from this experiment. The control supernatant was colorless and contained no soluble iron, indicating no dissolution of simulant at pH 10. The irradiated solution showed a trace of soluble iron corresponding to 0.2% dissolution of the simulant. Little or no cesium dissolution occurred in either solution.

The analyses for NO_3^- and NO_2^- in the 4 *M* NaOH and pH 10 solutions were consistent with the amounts initially added. The NO_3^- and NO_2^- concentrations in the 4 *M* NaOH control experiment were essentially those arising from dissolution of the In Farm 1 material, calculated to be 0.301 *M* and 0.100 *M*, respectively. However, a net conversion of NO_3^- to NO_2^- was observed during the gamma pit test. Similarly, the concentrations of these anions in the pH 10 control solution were the same as those added. The results of the two sets of experiments are compared in Table 4-3.

Additional experiments were conducted to investigate the solubility of $Na_2NiFe(CN)_6$ in caustic containing cesium ion. The purpose of these experiments was to determine whether cesium ion exchanges with sodium to form insoluble $Cs_2NiFe(CN)_6$ faster than the $Na_2NiFe(CN)_6$ will dissolve in NaOH forming soluble $Na_4Fe(CN)_6$ and insoluble $Ni(OH)_2$. Based on prior observations with cesium-containing materials, $Cs_2NiFe(CN)_6$ does not dissolve.

By monitoring soluble iron and soluble cesium ion as a function of time during a dissolution experiment, rates for these processes can be obtained.

In the two experiments performed, two 50 mL solutions, each containing 3 x 10^{-4} *M* $CsNO_3$, one containing 3 *M* NaOH, the other 4 *M* NaOH, were added to separate flasks containing 1 g of $Na_2NiFe(CN)_6 \bullet Na_2SO_4 \bullet 4.5H_2O$. The cesium concentration used was estimated from tank supernate sampling data. The reaction mixtures were stirred continuously, except during brief sampling periods. Solution samples were filtered and analyzed for iron and cesium by atomic absorption.

Table 4-3. Solution Analytical Data for Reaction Products from Hydrolysis of In Farm 1 Simulant.

	4 *M* NaOH, 90°C		pH 10, 60°C	
Analyte	Control	Gamma	Control	Gamma
NH_3	0.0109 *M*	0.0938 *M*	2.88 x 10^{-4} *M*	1.80 x 10^{-3} *M*
HCO_2^-	0.015 *M*	0.015 *M*	0.0039 *M*	0.0021 *M*
NO_3^-	0.288 *M*	0.146 *M*	1.063 *M*	0.937 *M*
NO_2^-	0.090 *M*	0.252 *M*	0.102 *M*	0.216 *M*
Fe	1,675 ppm	890 ppm	0.57 ± 0.68 ppm	4.34 ± 0.41 ppm
Cs	5.1 ppm	8.7 ppm	8.0 ± 1.8 ppm	0.52 ± 0.56 ppm

The results of these experiments were compared with earlier data from dissolution of the vendor material at pH 14 and data from dissolution of the In Farm 1 flowsheet material, which was precipitated with cesium. The data in Figure 4-6 show that, within the accuracy of the analytical method for iron, the concentration of base in these highly caustic solutions has little influence on dissolution and that the presence of 3 x 10^{-4} *M* cesium also does not greatly affect dissolution rate. Figure 4-7, however, shows that cesium is rapidly incorporated into the solid phase for both experiments with about 90% incorporated within 10 min. Future experiments at this cesium concentration will employ a larger solution volume.

Figure 4-6. Iron Concentration as a Function of Time.

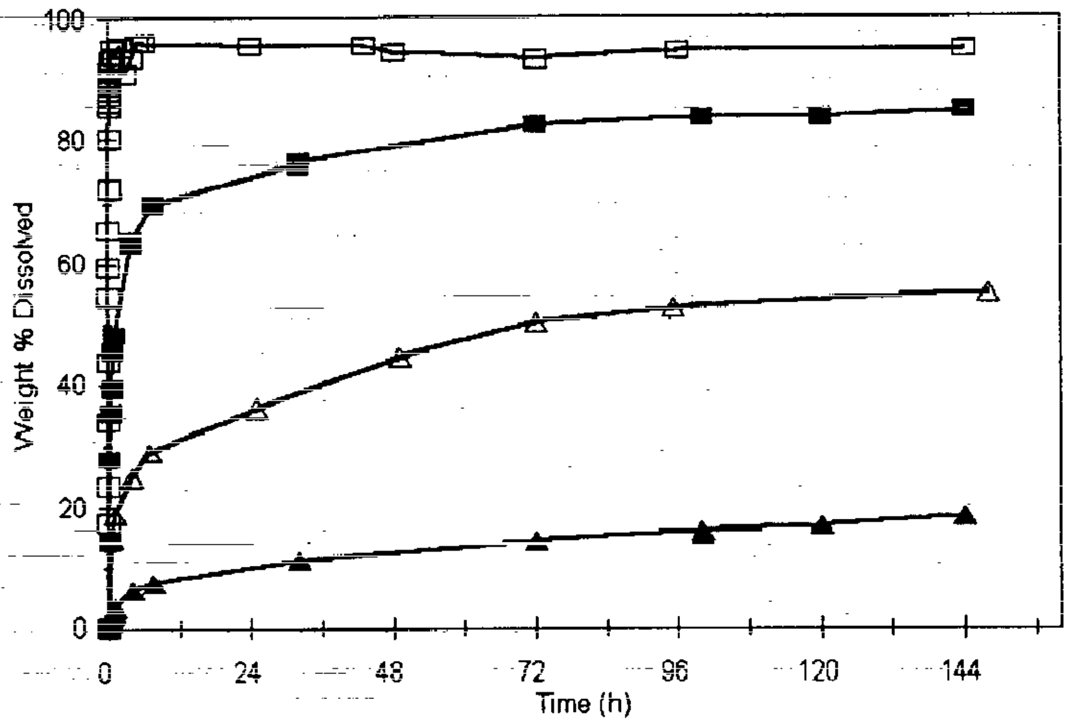
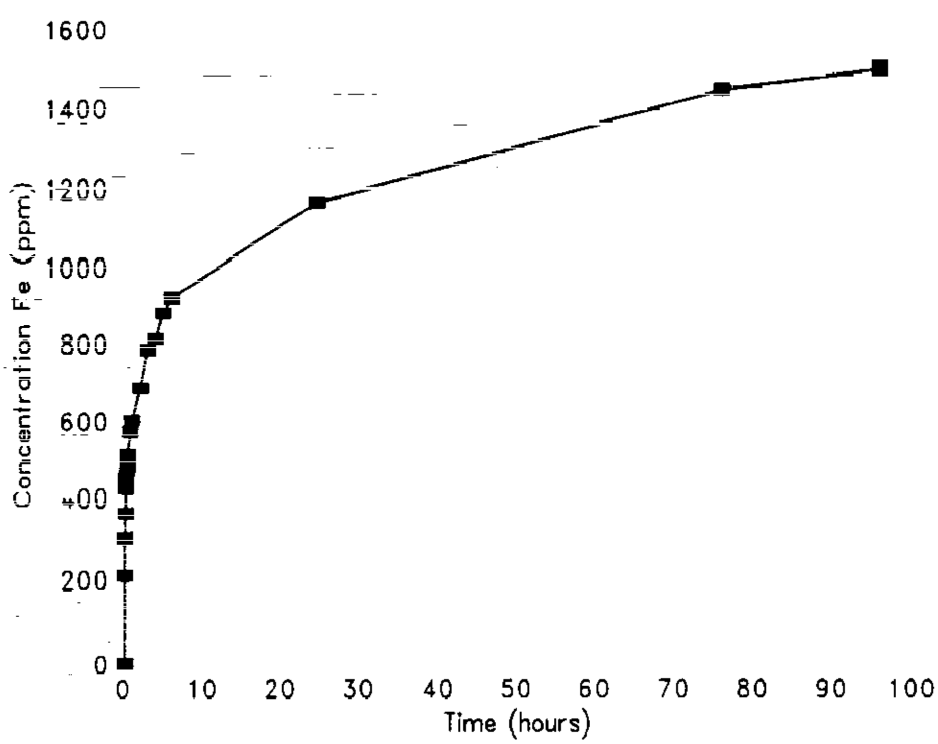


Figure 4-7. Cesium Concentration as a Function of Time.



Cyanide Speciation. A draft analytical procedure for the determination of major cyanide species [CN^-, $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$] in samples of ferrocyanide wastes has been developed. The methods employed are based on Fourier transform infrared spectroscopy (FTIR) and IC. Several ferrocyanide materials were analyzed using the draft analytical procedure and total cyanide analysis by a micro-distillation technique (Pool 1993). There was good agreement between all three methods. A report summarizing the procedure was publicly released this quarter (Bryan et al., 1993).

In preparation for evaluating the analytical procedure with actual ferrocyanide waste tank samples, FTIR equipment is being installed into a radiologically controlled laboratory. A radiologically controlled hood has been assigned for this task and a gas purge system has been installed.

Microconvection Modeling. In FY 1994, efforts will concentrate (1) on expanding a 2-D transport model developed last fiscal year to accommodate multiple species; and (2) coupling the transport code with an equilibrium chemistry model. The end goal of the modeling studies will be to quantitatively predict the amount of ferrocyanide that could have been solubilized and subsequently removed from the single-shell tanks from the fluid convection mechanisms that were identified last fiscal year. These convection mechanisms include buoyancy-aided flow caused by gradients in temperature and fluid chemical composition.

A literature review to determine the best approach for solving heat and multi-component reactive transport for tank waste problems indicates that an algorithm developed by NASA appears to offer the best approach. The difference equations that result from this algorithm maintain the space-time invariance of the original partial differential equations and thus minimize numerical diffusion which plagues conventional solution techniques for conservation laws. The algorithm will require a 2-D derivation before it can be used for modeling single-shell tanks.

Work was also started on modifying the free energy minimization code GMIN (Felmy 1990), which is a code for solving chemical equilibrium problems. The GMIN code is currently set up for single-pass input/output and must be modified for use as a subroutine that will be called hundreds or thousands of time in a transport simulation.

Cyanoferrate Solubility Study. Solubility studies are being conducted to investigate the solubility of $Na_xNiFe(CN)_6$ and $Cs_xNiFe(CN)_6$ as a function of Cs-ferrocyanide (for the solubility of $Cs_xNiFe(CN)_6$), Na-ferrocyanide (for $Na_xNiFe(CN)_6$), $NaNO_3$, and NaOH concentrations. This information will allow accurate prediction of the influence of chemical interactions and physical changes on the concentrations of these materials in the solid and the liquid phases of the ferrocyanide tank wastes. To obtain these data, the solubility of $Ni_2Fe(CN)_6$ as a function of either $NiCl_2$ or $Na_4Fe(CN)_6$ is being investigated.

Experiments have revealed that the solubility of $Ni_2Fe(CN)_6$ in both $NiCl_2$ and $Na_4Fe(CN)_6$ solutions is similar at three day and 18/19 day equilibration periods. This suggests that the dissolution kinetics of $Ni_2Fe(CN)_6$ are rapid and reach steady state concentrations in less than three days. The solubility of $Ni_2Fe(CN)_6$ in $NiCl_2$ shows an amphoteric behavior in which the solubility, in terms of soluble iron, first decreases and then increases with progressively increasing $NiCl_2$ concentrations. In contrast, the solubility of $Ni_2Fe(CN)_6$ in $Na_4Fe(CN)_6$, in terms of soluble Ni, shows a dramatic increase with increasing concentrations of $Na_4Fe(CN)_6$.

X ray diffraction analyses of the solid phases in contact with these solutions after 59-days of equilibration show that $Ni_2Fe(CN)_6$ was the only identifiable Ni containing solid in samples equilibrated with $Na_4Fe(CN)_6$. The solids from the $Ni_2Fe(CN)_6$ samples equilibrated with high $NiCl_2$ showed evidence of Ni substitution for Fe in the solids.

Reaction Kinetics Studies. During the last quarter of FY 1993 studies were conducted with an accelerating rate calorimeter (ARC) to measure Arrhenius kinetic parameters and to determine the thermal behavior of mixtures of sodium nickel ferrocyanide and nitrate and/or nitrite. The mixtures analyzed were: (1) a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite; (2) sodium nickel ferrocyanide and a 10 fold stoichiometric excess of sodium nitrate; (3) sodium nickel ferrocyanide and a 10 fold stoichiometric excess of sodium nitrite; and (4) a 10 fold stoichiometric excess of equimolar sodium nitrate and nitrite.

The near-stoichiometric mixture should exhibit the greatest reaction rate, because it has the least amount of inert material present to absorb heat. The studies using an excess of one reactant were performed to produce pseudo first order kinetic behavior. An insignificant amount of the excess reactant is consumed, making the reaction rate dependent on the limiting reactant.

An ARC test was performed on a 1.5 g sample of a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite using a temperature step of 5°C, and an exotherm identification criteria of a self-heat rate of 0.01°C/min. A reaction began at 180°C and continued at several different self-heating rates. The initial reaction slowed a couple of times before thermal runaway began at about 207°C. The reaction beginning at 180°C is associated with the rapid production of gases. The reaction beginning at 207°C is characterized by a drop in pressure, suggesting reaction of the product gases either with themselves or with the remaining solids. The pressure begins to increase again when the mixture self-heats to 227°C.

To obtain activation energies (E_a) and pre-exponential (A) parameters in the Arrhenius equation (Equation 1), it was assumed that a small amount of the reactants had been consumed at the beginning of the reaction; i.e. zero order kinetics existed at the start of a reaction. Based on this assumption, the least squares method was used to fit the initial portions of the reaction curves to the equation having the general form presented in Equation 2, where y = k, m = E_a/R, x = 1/T (with T in °K), and b = ln(A).

$$k = Ae^{-E_a/RT} \qquad \text{Equation 1}$$

$$\ln(y) = mx + b \qquad \text{Equation 2}$$

Table 4-4 shows the results of these calculations for the ARC test. The ARC results for the 10-fold nitrate mixture indicate that an exothermic propagating reaction begins at about 280°C. The pressure curve indicated that gases are being produced in the absence of an exothermic reaction, which suggests thermal decomposition or other endothermic reactions. At 240°C the pressure begins to drop rapidly indicating gas phase reactions or gas-solid reactions. Once the exothermic reaction begins at 280°C, the pressure increases rapidly in concert with the reaction or self-heat rate.

Table 4-4. Calculated Activation Energies and Pre-Exponentials for Selected Reaction Steps.

Start Temperature (°C)	E_a (kJ/mole)	A (s^{-1})
180	800	3.5×10^{90}
210	110	6.9×10^{10}
270	190	9.1×10^{17}

The thermal behavior of the mixture of sodium nickel ferrocyanide and a 10-fold stoichiometric excess of $NaNO_2$ revealed that the nitrite mixture begins reacting exothermically at 210°C, compared to 280°C for the nitrate mixture. The final propagating reaction step in the nitrite system begins at 250°C. Comparison of the two systems indicated that the nitrite system is more thermally sensitive than the nitrate system. The pressure curve again indicates that gas-phase or gas-solid reactions occur prior to the exothermic reaction step.

The thermal behavior of a mixture of sodium nickel ferrocyanide and a 10-fold stoichiometric excess of an equimolar $NaNO_3/NaNO_2$ mixture revealed that the first observed exothermic reaction occurs at 195°C, slightly earlier than the nitrite system. The second exothermic reaction is observed at 220°C, again lower than the nitrite system. This suggests that a system containing both nitrate and nitrite is slightly more sensitive to thermal initiation than a system containing only nitrate or nitrite.

- **Planned Work For Subsequent Months.** The aging study radiolysis and hydrolysis experiments will be continued using the most reactive ferrocyanide flowsheet simulant (In Farm 1). Temperature and pH will be evaluated during gamma pit radiolysis experiments to determine rates of hydrolysis under projected tank waste conditions as they existed for the years immediately after ferrocyanide waste scavenging. This work is expected to be completed in FY 1994.

  Cyanide speciation analytical methods development, including IC methods and solution IR methods, will continue until the validated techniques and procedures can be routinely applied to samples in the analytical laboratories at both PNL and Westinghouse Hanford Company. The studies will include the determination of interferences and corrections or work around that may be encountered in developing analytical methods for actual waste samples. Completion of this phase is expected by the end of FY 1994.

  Microconvection modeling studies have been expanded and information that contains key physical and chemical properties of waste as described above for FY 1994 will be assembled. This task is expected to be completed by September 30, 1994.

- **Problem Areas and Actions Taken.** None

- **Milestone Status.**

  - **September 30, 1994:** Issue the final PNL report, cleared for public release, on solution IR and IC cyanoferrate speciation activities and application for routine measurements in the analytical laboratory.

  - **September 30, 1994:** Issue the final PNL report, cleared for public release, on hydrolysis and radiolysis aging experiments with ferrocyanide waste materials.

  - **September 30, 1994:** Issue the final PNL report, cleared for public release, on microconvection modeling and the effects projected to have occurred in the tank waste from this phenomenon during more than 35 years of storage.

- **September 30, 1994:** Issue a report, cleared for public release, on FY 1994 solids speciation development and status with recommendations for future work and deployment in the analytical laboratories.

- **September 30, 1995:** Complete development of solids speciation methods using FTIR and Raman, and validation of techniques and procedures for routine application in the analytical laboratories. Issue a final report, cleared for public release, on this task's activities.

4.5.2 Ferrocyanide Propagation Studies

Ferrocyanide adiabatic calorimetry and propagation tests are continuing at FAI under contract to Westinghouse Hanford Company. The results of these tests are being used to help determine if Hanford Site ferrocyanide waste will ignite and burn to spread and involve additional waste from a potential ignition point, and to determine the potential for release of radioactive species under postulated accident conditions. Tests have been conducted with dried simulant to evaluate safety concerns associated with postulated hot spot accident conditions. The propagation velocity is a key parameter in determining safety consequences of postulated burns, including a potential radioactivity release from confinement.

Because the composition of the waste in the storage tanks varies and is not known at all locations, ranges of material compositions have been tested. Present work is focused on the T Plant and the more reactive In Farm 1 simulants. Sludge produced by the In Farm flowsheet was stored in four C Farm tanks and represents about 26% of the total ferrocyanide used in the Hanford scavenging processes. Sludge produced by the T Plant flowsheet was stored in three TY Farm tanks and represents about 8% of the total ferrocyanide used during the Hanford scavenging processes. Adiabatic calorimeter tests have also been initiated to assess possible organic fuel contributions to energy releases during ferrocyanide reactions.

The present concentration of ferrocyanide in the sludge is in question because ferrocyanide has been shown to hydrolyze in the presence of high pH waste (see Section 4.5.1). Initial sample results of C Farm tank waste indicate that the waste total cyanide concentrations are at considerably lower values than the In Farm simulants being tested (Simpson et al., 1993a, 1993b).

- **Progress During Reporting Period.** Adiabatic calorimeter tests using the Reactive System Screening Tool (RSST) and Vent Sizing Package (VSP)[4] calorimeters were completed at FAI on dried T Plant simulant (Fauske 1993c). The T Plant lower fraction simulant did not exhibit significant exothermic

[4]The RSST is a small scale calorimeter at FAI; the VSP is a larger size calorimeter that can handle much larger samples.

properties up to 350°C. The upper fraction of T Plant simulant behaved similar to the U Plant 2 bottom fraction simulant in exothermic behavior (Arrhenius type reaction). Onset temperature of the Arrhenius type reaction was 245°C in the RSST test. A peak temperature of 570°C and peak pressure of 3.3 atmospheres (gauge) were measured in the VSP test. The reaction properties exhibited in these tests indicate that the T Plant dried simulant is non-propagating.

Analysis of reaction products of four dried In Farm 1 bottom fraction simulant propagation tests were completed. For these tests dried and pulverized In Farm 1 bottom fraction material was loaded into 25 mm diameter by 80 mm long by 0.05 mm thick stainless steel cylinders. These test specimens were individually tested by igniting (using a 4 g Ba_2O_2 and Al mixture) in controlled argon atmospheres. In two of these tests the reaction gases were vented through filters to collect aerosols which were also analyzed. The reaction products from these tests have been analyzed by x ray diffraction, x ray fluorescence, IC, Inductively Coupled Plasma (ICP), atomic adsorption (AA), and FTIR analytical techniques.

Results indicate that significant identifiable crystalline reaction products include $NaFeO_2$, Na_2CO_3 (with and without a water of hydration), and Ni_3Fe. With the exception of test 1, little or no nitrate and nitrite were identified in the reaction products indicating that all had reacted or decomposed because of the high temperatures (>1250°C) produced.

Reaction product analysis by x ray fluorescence for each of the four tests, ICP, IC, FTIR, and AA are presented in Table 4-5. Preliminary evaluations of these results indicate that where the reaction temperatures exceeded 1050°C, the nitrate and nitrite were reacted or decomposed. The presence of sulfite and thiosulfate in the reaction products at the low quantities measured in three of the four tests suggests that the sulfide in nickel sulfide was oxidized to these products. Sodium and cesium were the major metallic constituents in the aerosol.

The fraction of cesium released from the reactions of tests 3 and 4 were determined to be 14 wt% for the 61°C initial temperature test and 22 wt% for the 120°C initial temperature test. These values were determined by summing the (1) aerosol collected on the filter papers; (2) the deposition on the aluminum foil lining (top, sides, and bottom) of the reaction chamber; and (3) the loose deposits at the bottom of the reaction chamber. The amount of released cesium collected as aerosol on the filters from vented gases ranged between 61 to 71%. Fractions of sodium, iron, and nickel released varied from 2.3 to 6.5%, 0.33 to 0.59%, and 0.45 to 0.80%, respectively, for the 60°C and the 120°C tests.

Table 4-5. In Farm 1 Bottom Fraction Simulant (Dried) Reaction Product Analysis.

Analyte	Weight Percent of Propagation Tests Reaction Products									
	Test 1, Initial Conditions 49.7 g, 61°C, 10 Atm		Test 2, Initial Conditions 49.8 g, 62°C, 51.7 Atm		Test 3, Initial Conditions 50.0 g, 61°C, 3.0 Atm			Test 4, Initial Conditions 50.0 g, 121°C, 3.2 Atm		
	29.7 g (Upper)	3.37 g (Lower)	20.5 g (Upper)	11.1 g (Lower)	Filter Aerosol	26.8 g (Upper)	7.05 g (Lower)	Filter Aerosol	19.3 g (Upper)	11.7 g (Lower)
Fe	7.3	5.5	10.5	6.0	0.32	9.4	3.6	0.30	11.6	3.1
Na	26.0	27.0	23.0	28.0	25.0	22.0	29.0	28.0	---	32.1
Ni	8.0	6.8	8.7		1.20	8.0	3.1	1.00	11.0	3.1
P	1.8	1.9	2.9	3.0	0.53	2.2	2.8	0.56	1.9	2.8
Cs	0.40	0.43	0.75	0.90	5.8	0.55	0.75	4.74	0.39	0.60
NO_2	<0.05	2.7	<0.05	<0.05	NA	<0.05	<0.05	NA	0.10	<0.02
NO_3	0.49	1.9	<0.02	<0.02	NA	<0.02	<0.02	NA	0.07	<0.02
PO_4	5.3	5.4	6.4	8.3	NA	6.0	8.3	NA	4.7	8.2
SO_4	5.8	6.4	0.14	0.22	NA	0.38	0.31	NA	2.4	3.9
SO_3	0.0	0.0	0.21	0.50	NA	0.27	0.31	NA	0.20	0.18
S_2O_3	0.0	0.0	0.40	0.41	NA	0.34	0.42	NA	0.71	1.1
Al	1.2	0.2	1.4	0.23	1.3	1.8	0.13	1.20	2.7	0.3
Ba	1.8	0.12	2.9	0.08	0.28	1.75	0.03	0.14	1.9	0.11

Notes: NA = Not Analyzed
Atm = Atmospheres Absolute Pressure

Adiabatic calorimetry tests have been initiated to determine the potential additional energy release contributions from low concentrations of organics which may be in the ferrocyanide waste. Three organics are to be evaluated: (1) sodium acetate representing an average energy producing organic carbon; (2) sodium stearate representing a maximum energy producing organic carbon; and (3) sodium oxalate representing a stable end product of degradation reactions believed to be occurring in waste tanks.

Contributory energy release for reactions of these organics are about 5.5 MJ/kg for sodium acetate, or sodium stearate and about 1 MJ/kg for sodium oxalate. The values were determined by FAI with appropriate adjustments for heat capacities on nitrates/nitrites in the test materials.

- **Planned Work for Subsequent Months.** Complete propagation screening tests with stoichiometric mixes to identify important parameters. Define additional parametric and ferrocyanide/organic tests to be conducted and have these initiated at FAI. Conduct dry out tests by simulating local heat generation in the sludge volume. Complete adiabatic calorimeter studies on organics.

- **Milestone Status.**

  - **January 31, 1993:** Completed pressure parametric and confined scoping aerosol/propagation tests on the most reactive flowsheet simulant at FAI (Fauske 1993a, Fauske 1993b).

  - **July 30, 1993:** Completed report on T Plant calorimetry and propagation tests and dry out tests (Fauske 1993c).

  - **September 30, 1993:** Complete report on stoichiometric scanning calorimeter tests. This report was completed by FAI in August 1993. The report will be prepared for public release and issued in February 1994.

  - **September 30, 1993:** Complete organic calorimetry scanning tests. These tests were completed on schedule and a report, cleared for public release, will be issued next quarter.

  - **December 15, 1993:** Complete theoretical evaluations on hot spots and tank waste dryout. Conduct confirmatory tests and provide a report that supports USQ closure. This report was completed by FAI in November 1993. The report will be cleared for public release next quarter.

  - **March 24, 1994:** Complete screening tests of In Farm 1 simulant at FAI by varying ferrocyanide and water compositions to define the empirical line that divides propagating and non-propagating mixtures (Postma et al., 1993) on the triangular diagram. Issue a report for public distribution.

May 31, 1994: Complete parametric aerosol tests at FAI, if required, that provide source terms for determining consequences of hypothetical ferrocyanide burns in a ferrocyanide tank.

September 30, 1994: Provide technical evaluations and analyses from FAI to resolve the hot spot issue. Issue a report to Westinghouse Hanford Company for public distribution.

September 30, 1995: Complete FY 1995 ferrocyanide calorimetry and propagation test program at FAI as specified by Westinghouse Hanford Company and prepare reports, available for public release, that support resolution of the Ferrocyanide Safety Issue.

4.6 EMERGENCY RESPONSE PLANNING

"The Board had recommended 'that an action plan be developed for the measures to be taken to neutralize the conditions that may be signaled by alarms.' Two types of measures are implied: actions to respond to unexpected degradation of a tank or its contents, and actions to be taken if an explosion were to occur. Your implementation plan stated that 'the current contingency plans . . . will be reviewed and revised if needed.' We do not consider that this proposed implementation of the Board's recommendation is adequately responsive. It is recommended that a written action plan founded on demonstrated principles be prepared as soon as possible, that would respond to indications of onset of abnormal temperatures or other unusual conditions in a ferrocyanide-bearing tank, to counter any perceived growth in hazard. A separate emergency plan should be formulated and instituted, covering measures that would be taken in event of an explosion or other event leading to an airborne release of radioactive material from the tanks, and that would protect personnel both on and off the Hanford Site. The Board believes that even though it is considered that the probability is small that such an event will occur, prudence dictates that steps be taken at this time to prepare the means to mitigate the unacceptable results that could ensue."

4.6.1 Action Plan for Response to Abnormal Conditions

The *Action Plan for Response to Abnormal Conditions in Hanford Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991a) was prepared in response to DNFSB recommendations. The action plan describes the steps to be taken if a temperature increase trend above the tank temperature baseline is measured in any of the ferrocyanide tanks. The document was revised in December 1991 and reissued as WHC-EP-0407, Rev. 1 (Cash and Thurman 1991b) to include the monitoring criteria and responses for abnormal levels of flammable and toxic gases, as well as the reporting requirements if established criteria are exceeded.

Also addressed in this section are actions in response to other abnormal conditions that might be encountered with the ferrocyanide tanks, such as a leak to the environment. Of the 20 tanks currently on the Ferrocyanide Watch List, 11 are classified as assumed leakers. Four of the assumed leaker tanks have not been interim stabilized. These four tanks and an additional sound tank still require some pumping to be classified as interim stabilized. Because this activity involves the Ferrocyanide USQ, SA and EA documentation must be authorization to pump these tanks must be granted by DOE.

- **Progress During the Reporting Period.** Both the SA and the EA for removing pumpable liquids from ferrocyanide tanks were submitted to DOE for review in September 1992. Comments were received on the documents in early January and they were revised and resubmitted at the end of January 1993. Additional comments were received on the SA and EA in July 1993. The EA has now been incorporated into the generic EA covering work on Watch List Tanks (see Section 3.0). The generic EA was submitted to DOE for approval in November 1993. The revised SA was resubmitted to DOE for final approval on November 30, 1993. A request for authorization for stabilization and emergency pumping of the ferrocyanide tanks was submitted to DOE.

- **Planned Work for Subsequent Months.** Interim stabilization of the five remaining ferrocyanide tanks will proceed after authorization is received from DOE. Each tank will undergo a readiness review prior to commencing pumping operations. The November 1993 submittal completes all actions required prior to authorization, unless DOE requests further action on the SA. Pumping of the tanks will be managed by Tank Farm Operations.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.** All milestones have been completed.

4.6.2 Response to an Airborne Release From a Ferrocyanide Tank

If a radioactive release from a ferrocyanide tank were to occur, it would be detected by one or more radiation monitoring systems. Significant airborne or ground surface releases that spread beyond the immediate tank or tank farm would be detected by the tank farm area radiation detectors. These monitoring systems are on all tank farms. The DOE and Westinghouse Hanford have analyzed the potential impacts of an event involving one of these tanks, and have taken additional steps so that emergency personnel can take mitigating actions in a timely fashion. These analyses resulted in development of the *Tank Farm Emergency Response Stabilization Plan* (WHC 1991) in March 1991. The plan includes predetermined mitigative actions for terminating the emergency phase and providing a transition to the recovery phase. Acknowledging that an event could range from minor to major releases, the plan addresses responses in four distinct and defined steps that cover the range of consequences. The *Stabilization Plan* provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste tank.

- **Progress During Reporting Period.** As noted in previous reports, all of the planned milestones for this task were completed.

- **Planned Work For Subsequent Months.** None planned.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.** All milestones have been completed.

5.0 PROGRAM SCHEDULES AND MILESTONES

Two sets of schedules (Figures 5-1 and 5-2) are presented in this section. Many of the program activities have changed over the course of the program and progress should be tracked against the new schedules presented here. The first set of schedules reviews milestones for FY 1991 through FY 1994; these have been statused through the period ending December 31, 1993. A status line was drawn showing the progress on each activity. Actions that have started or been completed are indicated by triangles that are filled in. Work indicated by open triangles has either not started or has not been completed. Similarily, actions which support completion of TPA milestones are indicated by open or closed diamonds.

The second set of schedules reviews out-year milestones for FY 1994 through the expected end of the program in FY 1997. The sequence and anticipated completion dates of the major milestones leading to safety issue resolution are presented. This report will be updated quarterly to track progress against these schedules.

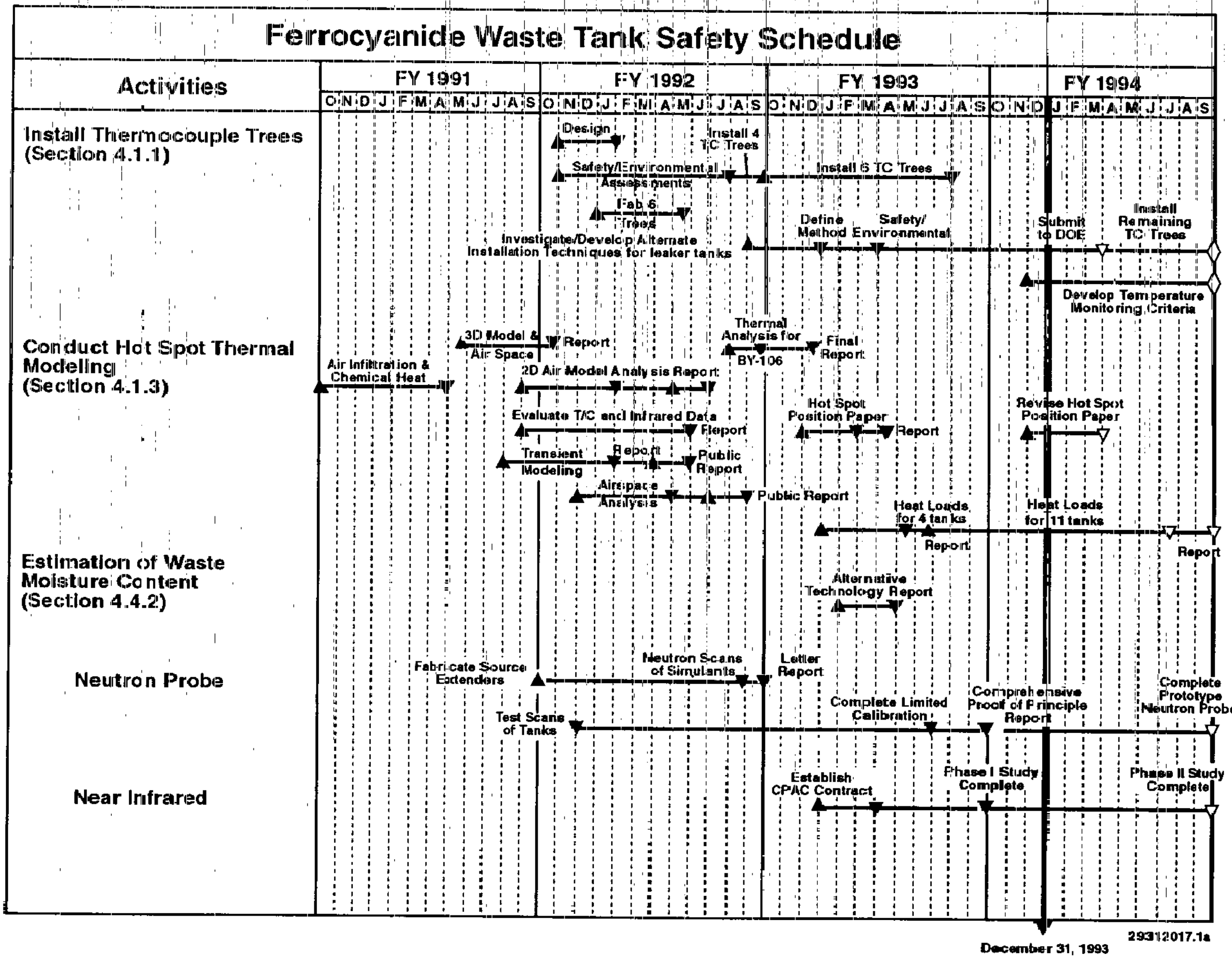


Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 1 of 4)

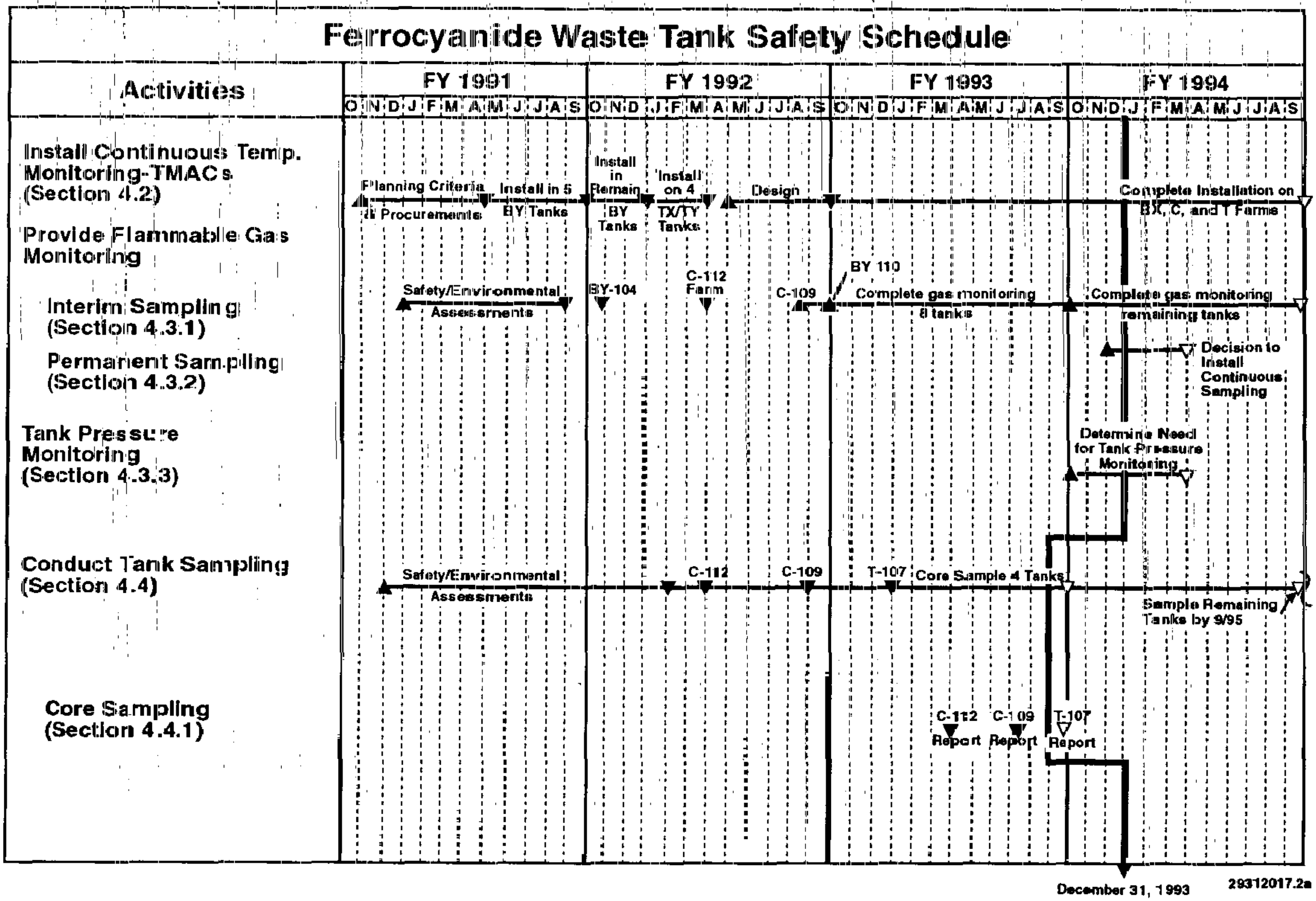


Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 2 of 4)

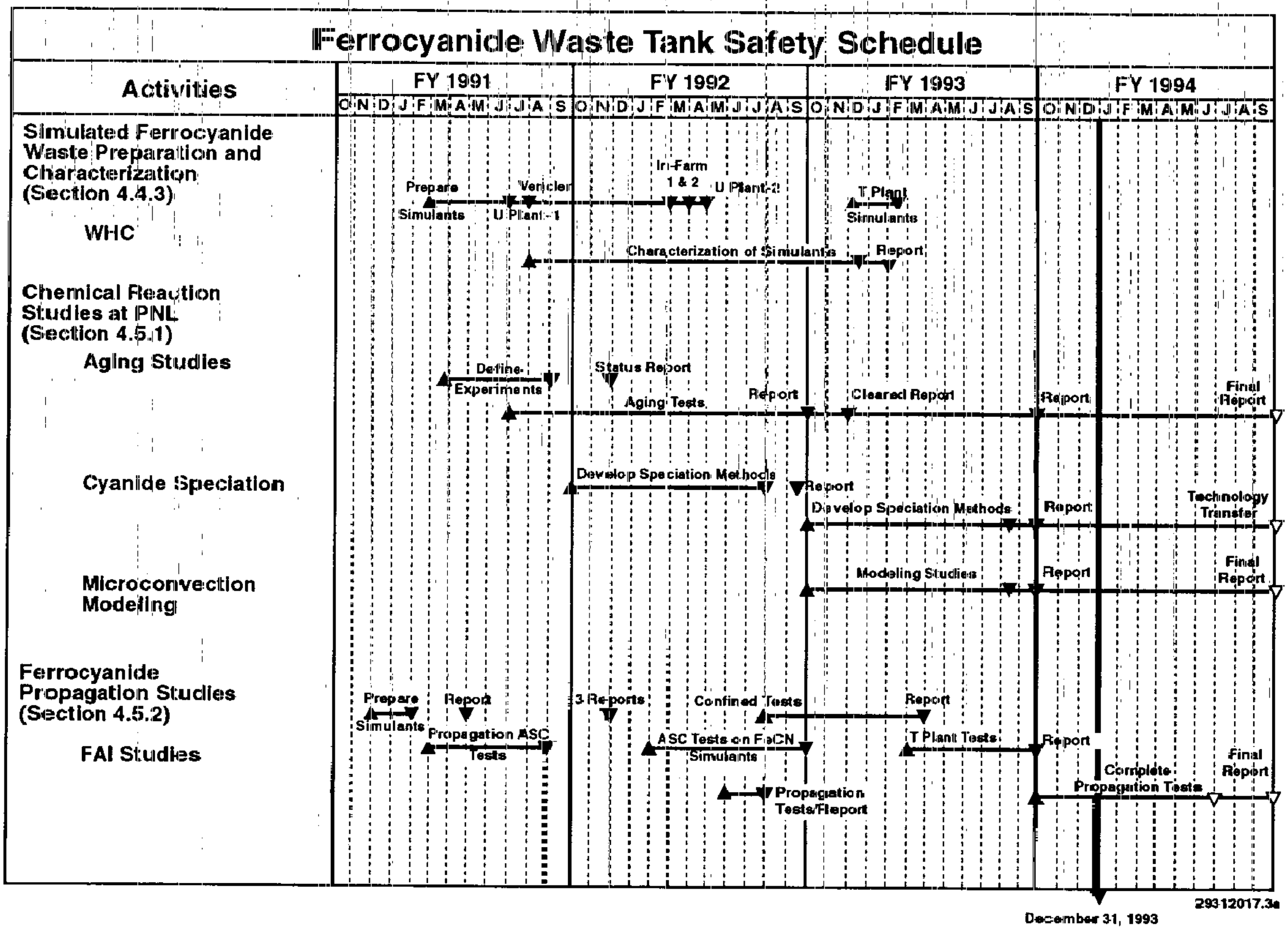


Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 3 of 4)

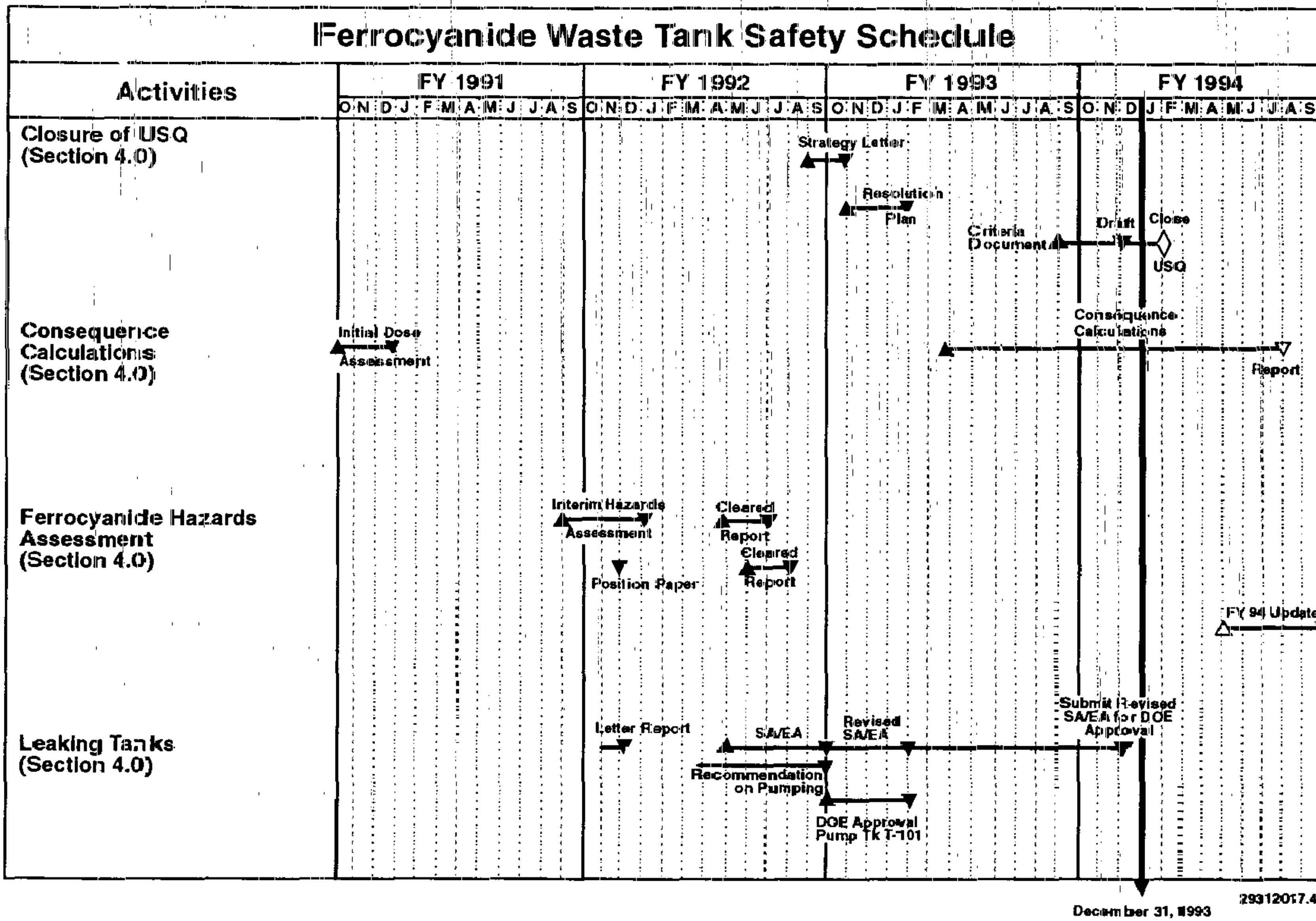


Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 4 of 4)

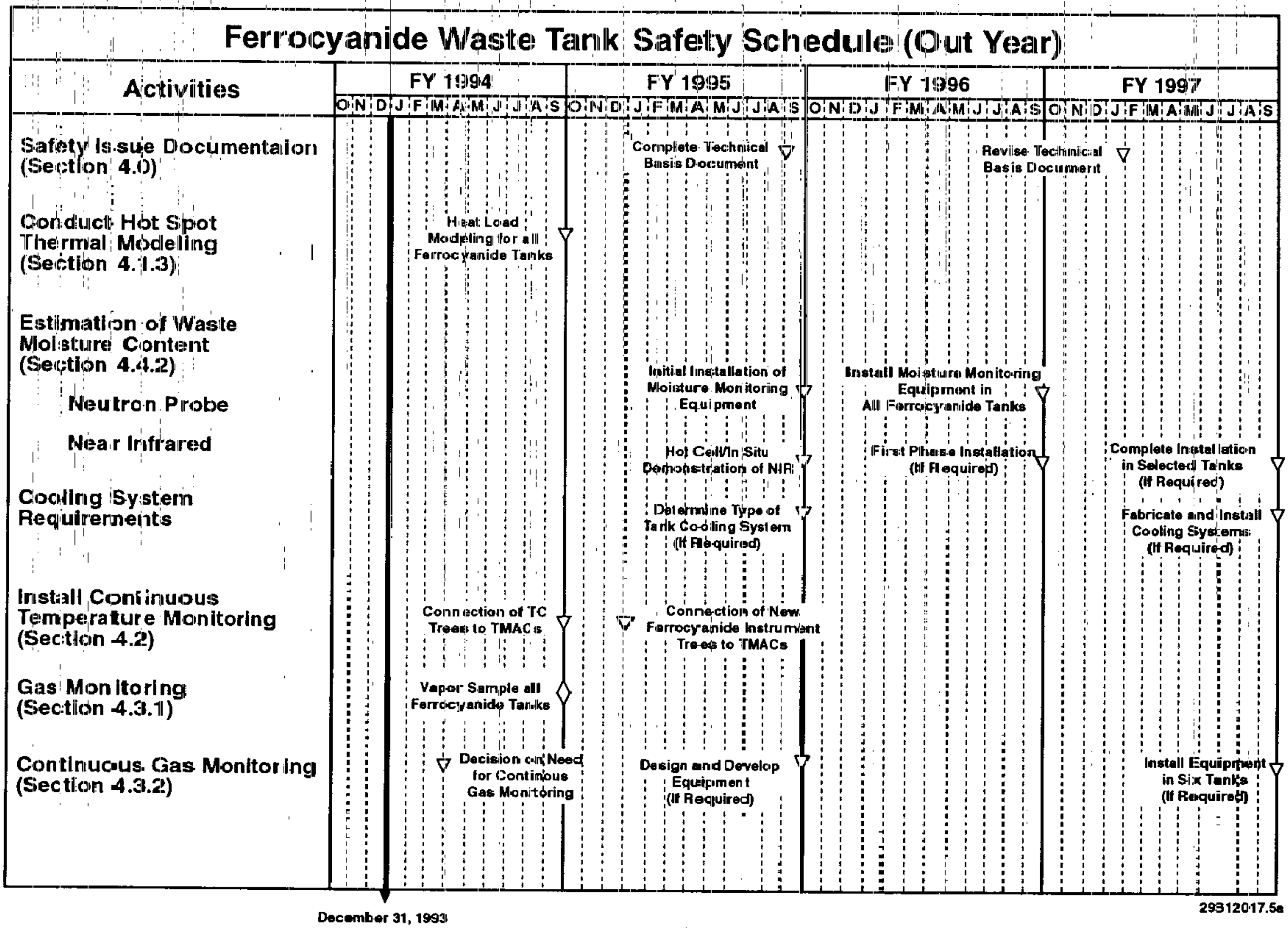


Figure 5-2. Ferrocyanide Waste Tank Safety Schedule (Out Year). (Sheet 1 of 2)

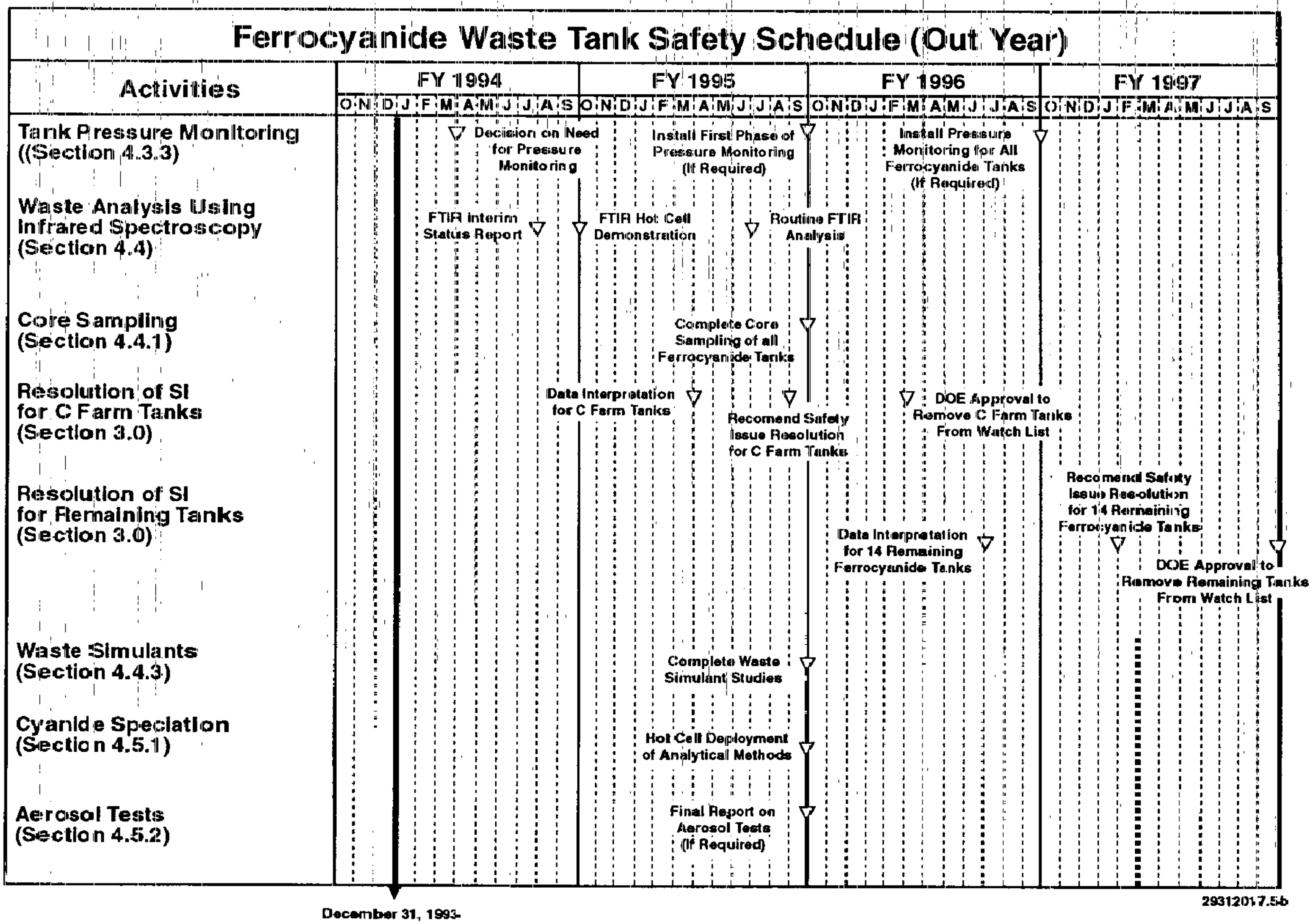


Figure 5-2. Ferrocyanide Waste Tank Safety Schedule (Out Year). (Sheet 2 of 2)

This page intentionally left blank.

6.0 REFERENCES

Borsheim, G. L., and B. C. Simpson, 1991, *An Assessment of the Inventories of Ferrocyanide Watchlist Tanks,* WHC-SD-WM-EP-133, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., R. J. Cash, and G. T. Dukelow, 1992, *Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7*, WHC-EP-0415, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., J. E. Meacham, R. J. Cash, and G. T. Dukelow, 1993a, *Program Plan for Evaluation of the Ferrocyanide Waste Tank Safety Issue at the Hanford Site*, WHC-EP-0721, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., J. E. Meacham, R. J. Cash, and B. C. Simpson, 1993b, *Ferrocyanide Safety Program: Rationale for Removing Six Tanks From the Safety Watch List*, WHC-MR-0429, Westinghouse Hanford Company, Richland, Washington.

Bryan, S. A., K. H. Pool, L. L. Burger, and R. L. Sell, 1993, *Cyanide Speciation Studies FY 1993 Annual Report*, PNL-8887, Pacific Northwest Laboratory, Richland, Washington.

Buck, J. W., C. M. Anderson, B. A. Pulsipher, P. J. Turner, J. J. Toth, R.J. Cash, G. T. Dukelow, and J. E. Meacham, 1993, *Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process*, WHC-EP-0728, Westinghouse Hanford Company, Richland, Washington.

Burger, L. L., and R. D. Scheele, 1988, *Interim Report, Cyanide Safety Studies*, PNL-7175, Pacific Northwest Laboratory, Richland, Washington.

Burger, L. L., 1989, *Complexant Stability Investigation, Task 1 - Ferrocyanide Solids*, PNL-5441, Pacific Northwest Laboratory, Richland, Washington.

Bussell, J. H., 1992, *Engineering Evaluation of Thermocouples in Ferrocyanide Watchlist Tanks*, WHC-SD-WM-ER-134, Rev 0 and Rev 0A, Westinghouse Hanford Company, Richland, Washington.

Cady, H. H., 1993, *Evaluation of Ferrocyanide/Nitrate Explosive Hazard*, LA-12589-MS, Los Alamos National Laboratory, Los Alamos, New Mexico.

Cash, R.J., 1991, *Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7,* WHC-EP-0415, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Cash, R. J., and J. Thurman, 1991a, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, WHC-EP-0407, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Cash, R. J., and J. Thurman, 1991b, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, WHC-EP-0407, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

Deaton, D. E., 1990, *Unusual Occurrence - Unreviewed Safety Questions Regarding Tanks Containing Ferrocyanide*, WHC-90-B003-R1 (Update 10-22-91), Westinghouse Hanford Company, Richland, Washington.

Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen, 1993, *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Tank Waste by Hot Spots*, WHC-EP-0648, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

DOE, 1986, *Safety of Nuclear Facilities*, DOE Order 5480.5, U.S. Department of Energy, Washington, D.C.

DOE, 1987, *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level, Transuranic and Tank Waste, Hanford Site, Richland, Washington*, DOE/EIS-0113, Vol. 1 through 5, U.S. Department of Energy, Washington, D.C.

DOE, 1991, *Unreviewed Safety Questions*, DOE Order 5480.21, U.S. Department of Energy, Washington, D.C.

DOE, 1994, *Recommendation 93-5 Implementaion Plan*, DOE/RL 94-0001, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Fauske, H. K., 1993a, *Summary Report on Parametric Pressure Propagation Tests TO127-1 and TO128-1*, WHC-EP-0661, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1993b, *Summary Report on 49L Ferrocyanide Aerosol Tests TO208-1 and TO209-1*, WHC-EP-0662, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1993c, *Adiabatic Calorimetry (RSST and VSP) Tests With Synthetic T Plant Flow Sheet Material*, (letter to R. J. Cash, dated July 28, 1993), Fauske and Associates, Inc., Burr Ridge, Illinois.

Felmy, A. R., 1990, *GMIN: A computerized Chemical Equilibrium Model Using a Constrained Minimization of the Gibbs Free Energy*, PNL-7281, Pacific Northwest Laboratory, Richland, Washington.

FR, 1990, "Implementation Plan for Recommendation 90-3 at the Department of Energy's Hanford Site, Washington," *Federal Register*, Defense Nuclear Facilities Safety Board Recommendation 90-7, Vol. 55, No. 202, pp. 42243 - 42244.

Grumbly, T. P., 1993, *Strategy for [Ferrocyanide] Safety Issue Resolution*, (letter to J. T. Conway, Chairman, Defense Nuclear Facilities Safety Board, dated August 25, 1993), U.S. Department of Energy, Washington, D.C.

McLaren, J. M., 1993, *Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104*, WHC-EP-0669, Westinghouse Hanford Company, Richland, Washington.

McLaren, J. M. and R. J. Cash, 1993, *Ferrocyanide Safety Program: Heat Load and Thermal Characteristics Determination for Selected Tanks*, WHC-EP-0638, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., R. J. Cash, and G. T. Dukelow, 1993a, *Quarterly Report on Defense Nuclear Facilities Safety Board Recommendation 90-7 for the Period Ending September 30, 1993*, WHC-EP-0474-10, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., H. Babad, and H. Toffer, 1993b, *Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools*, WHC-EP-0658, Westinghouse Hanford Company, Richland, Washington.

O'Leary, H. R., 1993, *Hanford Tank Waste Remediation System Safety Initiatives*, U.S. Department of Energy, Washington, D.C., September 17, 1993.

Peach, J. D., 1990, *Consequences of Explosion of Hanford's Single-Shell Tanks are Understated*, (letter B-241479 to M. Synar, Chairman, Environment, Energy, and Natural Resources Subcommittee, Committee on Government Operations, House of Representatives), GAO/RCED-91-34, U.S. General Accounting Office, Washington, D.C., October.

Pool, K. H., 1993, *Total Cyanide Analysis of Tank Core Samples: Analytical Results and Supporting Investigations*, PNL-8858, Pacific Northwest Laboratory, Richland, Washington.

Postma, A. K., J. E. Meacham, G. S Barney, G. L. Borsheim, R. J. Cash, M. D. Crippen, D. R. Dickinson, J. M. Grigsby, D. W. Jeppson, M. Kummerer, J. M. McLaren, C. S. Simmons, and B. C. Simpson, 1993, *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*, WHC-EP-0691 [Draft], Westinghouse Hanford Company, Richland, Washington.

Public Law 101-510, Section 3137, *Safety Measures for Waste Tanks at Hanford Nuclear Reservation.*

RHO, 1986, *Single-Shell Tank Isolation Safety Analysis Report*, SD-WM-SAR-006, Rev. 2, Rockwell Hanford Operations, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0688, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Toffer, H., 1993, *Riser Survey for New Liquid Observation Well (LOW) and LOW Material Considerations for Neutron Probe Applications*, (internal memo, to G. T. Dukelow, December 27, 1993), Westinghouse Hanford Company, Richland, Washington.

Veltkamp, D., 1993, *CPAC Moisture Study: Phase I Report on the Study of Optical Spectra Calibration for Moisture*, WHC-SD-WM-ER-288, Rev. 0, Westinghouse Hanford Company, Richland, Washington. Contract Number MLR-SVV-562951, Center for Process Analytical Chemistry, University of Washington, Seattle, Washington.

Wagoner, J. D., 1993, Letter, J. D. Wagoner, RL, to T. M. Anderson, WHC, "Approval of Hanford Site Tank Farm Facilities Interim Safety Basis," ADT:TOB 93-TOB-209, dated November 18, 1993, U. S. Department of Energy, Richland, Washington.

Watson, W. T., 1993, *Proof of Principle Report for In-Tank Moisture Monitoring Using an Active Neutron Probe*, WHC-EP-0695, Westinghouse Hanford Company, Richland, Washington.

WHC, 1991, *Tank Farm Stabilization Plan for Emergency Response*, WHC-SD-PRP-TI-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

WHC, 1992, *Management Requirements and Procedures*, "Identification and Resolution of Unreviewed Safety Questions," WHC-CM-1-3, Section 5.12, Westinghouse Hanford Company, Richland, Washington.

Wood, S. A., 1993, *Gas Space Analysis For Tank C-109*, WHC-SD-WM-ER-183, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.

APPENDIX A

FERROCYANIDE TANKS

This page intentionally left blank.

Table A-1. Summary of Contents and Status of Ferrocyanide Tanks[a].

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (Btu/h)[c]	Maximum temp. (°C)	Maximum temp. (°F)	Status of tanks[d]
BX-102	96	< 1	2,800	19	67	IS; AL
BX-106	46	< 1	2,500	19	67	NS; Sound
BY-103	400	66	5,500	28	82	NS; AL
BY-104	406	83	8,700	53 46[e]	128 114	IS; Sound
BY-105	503	36	8,700	45 48	113 119	NS; AL
BY-106	642	70	10,100	54	129	NS; AL
BY-107	266	42	8,900	34	94	IS; AL
BY-108	228	58	9,200	43	110	IS; AL
BY-110	398	71	6,900	47 43[e]	117 109	IS; Sound
BY-111	459	6	5,500	30 29[e]	86 84	IS; Sound
BY-112	291	2	6,100	29 32[e]	84 90	IS; Sound
C-108	66	25	6,000	24 29[e]	76 85	IS; Sound
C-109	66	30	7,000	26 26[e]	78 78	IS; Sound
C-111	57	33	6,400	24	75	IS; AL
C-112	104	31	7,500	28 27[e]	83 81	IS; Sound
T-107	180	5	3,000	22	71	NS; AL
TX-118	347	< 3	4,600	25	77	IS; Sound

Table A-1. Summary of Contents and Status of Ferrocyanide Tanks[a].

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (Btu/h)[c]	Maximum temp. (°C)	(°F)	Status of tanks[d]
TY-101	118	23	3,100	20	68	IS; AL
TY-103	162	28	4,000	21	70	IS; AL
TY-104	46	12	3,000	20	68	IS; AL

[a] Reflects removal of four ferrocyanide tanks from Watch List in July 1993. Tank information and temperature data as of December 1993.

[b] Inventories from Borsheim and Simpson, 1991.

[c] Heat load values from Table 7-1 in Crowe et al. 1993.

[d] IS - Interim Stabilized Tank; NS - Not Stabilized; AL - Assumed Leaker Tank; Sound - Non-Leaking Tank.

[e] Temperatures recorded for new thermocouple trees.

Table A-2. Ferrocyanide Tank Vapor Sampling Summary

Tank[1]	Date Sampled	Flamm (% LFL)	Org. Vapor (ppm)	Ammonia (ppm)	HCN/CN (ppm)	Hydrazine (ppm)	Nitrous Gas (ppm)
241-BY-104	10/16/91 - 10/30/91	1.0	37.2	250	<2	>3.0[2]	>10
241-C-112	03/09/92 - 03/18/92	<1.0	<0.2	<5	<2	<0.2	<2
241-C-109	08/26/92	<1.0	---	<5	<2	<0.2	<0.5
241-BY-110	09/27/92	<1.0	350	612[3]	<2	<0.2	<0.5
241-T-107	10/22/92	<1.0	24	203	<2	<0.2	<0.5
241-BY-111	03/25/93	<1.0	6.3	10.2	<2	<0.2	<0.5
241-BY-112	03/26/93	<1.0	5.9	10.0	<2	<0.2	<0.5
241-BX-106	06/17/93	<1.0	12	17.9	<2	<0.2	<0.5
241-C-108	07/23/93	<1.0	1.2	<2	<2	<0.2	<0.5
241-TX-118	07/28/93	<1.0	0.3	10.1	<2	<0.2	0.5
241-C-111	08/11/93	<1.0	<0.2	<2	<2	<0.2	<0.5

[1]Maximum reported values for sampling effort
[2]High reading due to ammonia interference
[3]Approximation due to concentration exceeding Dräger tube range

This page intentionally left blank.

APPENDIX B

METRIC CONVERSION CHART

This page intentionally left blank.

Table B-1. Metric Conversion Chart.

Into Metric			Out of Metric		
If You Know	Multiply By	To Get	If You Know	Multiply By	To Get
Length			Length		
in.	2.54	cm	mm	0.04	in.
ft	30.48	cm	cm	0.4	in.
Mass (weight)			Mass (weight)		
lb	0.453515	kg	kg	2.2	lb
Volume			Volume		
gal	3.78541	L	L	0.264172	gal
Temperature			Temperature		
Fahrenheit (°F)	Subtract 32 then multiply by 0.55555...	Celsius (°C)	Celsius (°C)	Multiply by 1.8, then add 32	Fahrenheit (°F)

This page intentionally left blank.

DISTRIBUTION

Number of copies	
OFFSITE	
6	U.S. Department of Energy EM-35, Trevion II Washington, D.C. 20585 J. V. Antizzo
1	U.S. Department of Energy Savannah River Operations Office P.O. Box A Aiken, South Carolina 29808 T. C. Temple
1	C. S. Abrams 1987 Virginia Idaho Falls, ID 83404
1	D. O. Campbell 102 Windham Road Oak Ridge, TN 37830
1	F. N. Carlson 6965 North 5th West Idaho Falls, ID 83401
1	D. T. Oakley 555 Quince Orchard Road Gaithersburg, MD 20878
1	A. K. Postma 3640 Ballard Road Dallas, OR 97338
1	W. R. Prindle 1556 Crestline Drive Santa Barbara, CA 93105

DISTRIBUTION (cont)

Number of copies	
OFFSITE	
1	A. Schneider 5005 Hidden Branches Drive Dunwoody, GA 30338
1	Air Products & Chemicals, Inc. 7201 Hamilton Blvd Allentown, PA 18195-1501 G. E. Schmauch
1	Battelle Columbus Laboratories 505 King Avenue Columbus, OH 43201-2693 J. A. Gieseke
1	Brookhaven National Laboratory Upton, NY 11973 K. K. Bandyopadhyay
1	Design Science, Inc. 163 Witherow Road Sewickley, PA 15143 G. Powers
1	Fauske and Associates, Inc. 16W070 W. 83rd St. Burr Ridge, IL 60521 H. K. Fauske
1	Florida State University Department of Chemistry B-164 Tallahassee, FL 32306 G. R. Choppin

DISTRIBUTION (cont)

Number of copies

OFFSITE

1	Harvard University 295 Upland Avenue Newton Highlands, MA 02161 M. W. First
1	Hazards Research Corporation 200 Valley Road, Suite 301 Mt. Arlington, NJ 07856 C. Grelecki
1	Lawrence Livermore National Laboratory P. O. Box 808, L-221 Livermore, CA 94550 B. C. Hudson
4	Los Alamos National Laboratory P.O. Box 1663 Los Alamos, NM 87545 S. F. Agnew S. W. Eisenhawer T. E. Larson L. H. Sullivan
1	MIT/Department of Nuclear Engineering 77 Massachusetts Ave. Room 24-102 Cambridge, MA 02139 M. S. Kazimi

DISTRIBUTION (cont)

Number of copies

OFFSITE

1	Nuclear Consulting Services, Inc. P.O. Box 29151 Columbus, OH 43229 J. L. Kovach
1	Oak Ridge National Laboratory P.O. Box 2008 7930, MS-6385 Oak Ridge, TN 37831-6385 E. D. Collins
1	P.O. Box 2008 MS-6495 Oak Ridge, TN 37831-6495 C. W. Forsberg
1	Oak Ridge National Laboratory (cont) P.O. Box 2009 9108, MS-8088 Oak Ridge, TN 37831-8088 T. S. Kress
1	Rice University 5211 Paisley Houston, TX 77096 A. S. Veletsos
1	Sandia National Laboratory P.O. Box 5800 Albuquerque, NM 87185 S. E. Slezak

DISTRIBUTION (cont)

Number of copies	
OFFSITE	
3	Science Applications International Corporation Trevion I, Suite 300 20500 Century Blvd Germantown, MD 20874
	R. S. Daniels (3)
1	State of Washington Department of Ecology P. O. Box 47600 Olympia, WA 98504-7600
	M. T. Gordon
1	University of South Carolina Department of Electrical and Computer Engineering Swearingen Engineering Center Columbia, SC 29208
	J. S. Byrd
1	University of Washington Center for Process Analytical Chemistry Chemistry Department BG-10 Seattle, WA 98195
	B. R. Kowalski
1	Vanderbilt University P.O. Box 1596, Station B Nashville, TN 37235
	F. L. Parker

DISTRIBUTION (cont)

Number of copies

OFFSITE

15	U.S. Department of Energy, Richland Field Office	
	R. F. Christensen (4)	R3-72
	R. E. Gerton (7)	R3-72
	A. G. Krasopoulos	A4-81
	Public Reading Room	H2-53
	RL Docket File (2)	H5-36
10	Pacific Northwest Laboratory	
	R. T. Allemann	K7-15
	S. A. Bryan	P7-25
	A. R. Felmy	K6-82
	B. M. Johnson	K1-78
	M. A. Lilga	P8-38
	B. P. McGrail	K2-38
	R. D. Scheele	P7-25
	G. F. Schiefelbein	P8-38
	D. M. Strachan	K2-44
	Hanford Technical Library	P8-55
49	Westinghouse Hanford Company	
	H. Babad	R2-78
	G. A. Barnes	H5-09
	J. B. Billetdeaux	R2-08
	D. C. Board	S1-57
	G. L. Borsheim	R2-11
	S. R. Moreno	B3-06
	R. J. Cash (2)	R2-78
	M. D. Crippen	L5-31
	G. M. Christensen	H4-21
	D. R. Dickinson	L5-31
	G. T. Dukelow	R2-78
	S. J. Eberlein	L5-55
	J. M. Grigsby	H4-62
	H. D. Harmon	R2-52

DISTRIBUTION (cont)

Number of copies

OFFSITE

Westinghouse Hanford Company (cont)

	D. A. Healey	T4-07
	J. M. Held	R3-09
	M. N. Islam	R3-08
	D. W. Jeppson	L5-31
	N. W. Kirch	R2-11
	C. A. Kuhlman	B3-30
	M. Kummerer	H4-62
	J. D. McCormack	L5-31
	J. M. McLaren	H0-34
	J. E. Meacham	R2-78
	N. J. Milliken	H4-62
	T. L. Moore, Sr	H5-09
	A. F. Noonan	B1-40
	M. A. Payne	R2-50
	R. S. Popielarczyk	R1-30
	R. W. Reed	R1-51
	F. R. Reich	L5-63
	C. P. Schroeder	L7-06
	B. C. Simpson	R2-12
	J. P. Summerhays	R2-85
	H. Toffer	H0-38
	W. T. Watson	H0-38
	W. D. Winkelman	L5-55
	D. D. Wodrich	R2-79
	D. D. Wodrich	R2-85
	W. F. Zuroff	S6-85
	Central Files	L8-04
	Document Processing and Distribution (2)	L8-15
	EDMC	H6-08
	Information Release Administration (3)	R1-05
	TFIC	R1-20

This page intentionally left blank.

DISTRIBUTION (cont)

Number of copies

OFFSITE

Westinghouse Hanford Company (cont)

D. A. Healey	T4-07
J. M. Held	R3-09
M. N. Islam	R3-08
D. W. Jeppson	L5-31
N. W. Kirch	R2-11
C. A. Kuhlman	B3-30
M. Kummerer	H4-62
J. D. McCormack	L5-31
J. M. McLaren	H0-34
J. E. Meacham	R2-78
N. J. Milliken	H4-62
T. L. Moore, Sr	H5-09
A. F. Noonan	B1-40
M. A. Payne	R2-50
R. S. Popielarczyk	R1-30
R. W. Reed	R1-51
F. R. Reich	L5-63
C. P. Schroeder	L7-06
B. C. Simpson	R2-12
J. P. Summerhays	R2-85
H. Toffer	H0-38
W. T. Watson	H0-38
W. D. Winkelman	L5-55
D. D. Wodrich	R2-79
D. D. Wodrich	R2-85
W. F. Zuroff	S6-85
Central Files	L8-04
Document Processing and Distribution (2)	L8-15
EDMC	H6-08
Information Release Administration (3)	R1-05
TFIC	R1-20

THIS PAGE INTENTIONALLY
LEFT BLANK